Commentary

FOOD FOR THE FUTURE

The subjects covered at the British Association meeting were diverse as ever, ranging from the point of view of the octopus to the structure of the universe, but through all the sections ran one theme which culminated in the whole day symposium on World Food and Population. A new section, Sociology, most suitably made its appearance this year; together with the economist the sociologist has a most important part to play in the raising of the world-wide standard of living.

Look at the appalling figures: 60 per cent of the world's population receives less than 2200 calories a day, 69 per cent less than 2400 and the *minimum* satisfactory intake is about 2700 calories a day. And these figures do not take into account the appalling protein, mineral and vitamin deficiencies in the standard diets of the undernourished. Meanwhile, according to Professor D. V. GLASS of the London School of Economics, the population of the world is increasing at rates from 0·9 per cent per annum in Western Europe to 2·4 per cent in Latin America, probably rising to 2·8 per cent by 1975 (a 2·8 per cent annual rise means that a population doubles itself in twenty-five years). He prophesied that between 1960 and 2000 the population of the world could rise from 2500 million to 6000 million.

Two major problems must therefore be tackled: the adequate feeding of the present and the potential future population of the world and the controlling of the enormous rate of population increase.

Many solutions for the former were discussed. It was emphasized again and again, and from many different points of view, that with modern techniques the world's food production could be increased enormously. Even in Britain where we are getting some of the highest yields of food crops per acre in the world, we were told that it is possible to increase our production of acceptable food by at least 50 per cent. In India, Dr RICHARDSON of the Central Agricultural Control, I.C.I., estimated that by using fertilizers, better irrigation, improved varieties, *etc.*, average yields of paddy rice per acre could be increased from 1140 lbs to 2700 lbs and of wheat from 660 lbs to 2000 lbs. The immediate response to fertilizers alone is 52 per cent increase for rice and 45 per cent for wheat. Even in the United States only half the cultivable land is so used and still there is an enormous surplus of wheat, much of which is given to the underdeveloped countries. Sir Alexander FLECK summarized the main methods of improving agricultural output under five headings: extension of area under cultivation; irrigation; fertilization; substitution and rotation of crops; mechanization; and increased efficiency. He also emphasized that the food produced must be used to maximum advantage employing modern techniques of food processing, manufacture and distribution.

It is development within the countries themselves which is the crux of the matter. Western economists, sociologists, and agriculturalists may make surveys and recommendations and external agencies may offer economic aid, but little improvement will take place unless there is an appreciation within the countries concerned of the importance of attracting the trained technologist, and in particular the indigenous technologist. At all levels the expert should be encouraged to introduce up-to-date agricultural and industrial techniques, adapt them to local conditions and, above all, educate and encourage the local people to use them. Outside assistance can only be a temporary solution and the maximum use must be made of it to develop the countries economically.

Slowing down the rate of population increase is even more difficult; in effect this means reducing the birth rate or survival rate and short of war or large-scale natural catastrophes mortality will continue to fall. With opposition from religious and political groups there is at present little likelihood of widespread instruction in contraceptive techniques, but even the Roman Catholic Church does appear to be slightly changing its ground on this subject and the development of oral contraceptives should greatly speed up the widespread adoption of birth control. But under present circumstances even the widespread use of contraceptives is unlikely to make a marked difference immediately as the mortality rate is dropping so rapidly that the population would still increase, as in Western Europe and North America. Professor GLASS said that with the lowering of the death rate in India by modern medical techniques the expectation of life could be raised from 32 in 1951 to 52 in 1981, implying a possible doubling of numbers in a generation. With even a 50 per cent fall in fertility between 1956 and 1981 India's numbers would still increase by over 200 millions by 1986.

The atmosphere of the meeting was not one of gloom, however, and one hopes that neither was it over-optimistic in assuming that the technological developments are adequate to meet the situation. Certainly the emphasis must now be on education and administration.

METHODS OF PRESERVING FOOD

other than Fermenting, Freezing or Canning

F. C. WEBB

Lecturer in Biochemical Engineering, University College London

Dr Webb concludes the Biochemical Engineering series by describing various methods of preserving food which have not been covered in previous articles. Reprints of all the articles in this series can be obtained from Butterworths, 4/5 Bell Yard, London, W.C.2.

MANY factors contribute to our having seasonal foods throughout the year and over wide areas but chief amongst them is the ability to store perishable foods in a fresh condition for considerable periods of time, either for normal transport and marketing requirements or sometimes far longer.

Reduced Temperature Preservation

Chilling plays a considerable part in many operations, firstly by slowing up all forms of chemical action taking place and secondly by inhibiting microbial growth. In many respects these are equivalent, but whereas chemical processes, usually centred round enzymic action slow up two to three times for every 10°C temperature drop, a number of micro-organisms stop multiplying altogether when approaching freezing point and reach a state of very low metabolic activity.

A particularly interesting example of man's control over metabolic processes is hard fruit storage—mainly applying to apples and pears. As picked they are living units with complex enzymically controlled reactions continuing in them which oxidize carbohydrates to carbon dioxide and water for their energy requirements. The whole level of metabolic activity can be slowed down by cooling, but also, since this oxidation is essentially reversible and subject to mass action laws, the overall rate can be further reduced by allowing the level of carbon dioxide to accumulate and that of oxygen to fall. These two methods applied together can be used to extend the normal storage period very appreciably to several months, but cannot be applied to excess as undesirable side reactions set in. British D.S.I.R. stations have done most of the fundamental work on this problem and list optimum conditions for different varieties of fruit. Thus Cox's Orange Pippins require 5 per cent carbon dioxide and 3 per cent oxygen at 39°F, while Bramley's Seedling stores longest with 9 per cent carbon dioxide and 12 per cent oxygen and more than 60,000 tons of fruit in England alone can be stored under these conditions. The design of these stores is a good example of applied biochemical engineering, embodying the construction of a relatively gas-proof, insulated chamber, fitted with a circulating refrigerated air system and usually a gas scrubbing plant to absorb excess CO_2.

A further interesting refinement of this principle is the controlled ripening of bananas and other fruit by small concentrations of ethylene.

These methods applied to fruit are, of course, very similar to those used for meat, but in this case, the temperature is held on the verge of freezing which enables the meat to be kept in good condition for several weeks. By adding a small percentage of carbon dioxide, this period can be further extended.

Control of Moisture Level

Satisfactory bulk storage of most biological materials is a function not only of temperature but also humidity, and this must generally be arranged so that at equilibrium in the enclosed store it is below the level at which active growth can take place. In the case of seeds, this may be actual germination or 'sprouting' but with most other products the humidity must be such that microbiological growth cannot occur. Biological items differ widely in composition but usually contain proteins, polysaccharides and various sugars, most of which have a strong affinity for water. This is absorbed or bound so strongly that it does not exert its usual vapour pressure, *i.e.* its 'activity' in the thermodynamic sense is well below unity. Also, unlike water of crystallization, the adsorption curve is smooth and progressive and the first few per cent often cannot be removed without damaging the material. Curves can be drawn relating percentage H_2O with equilibrium relative humidity as shown in *Figure 1*.

It will be seen that corn and indeed most cereals equilibrate at 50 per cent r.h. when containing about 12 per cent moisture.

Now the water activity can be assumed to be equal to the fractional r.h. and under normal conditions the lowest activities at which micro-organisms can

grow are known, ranging from 0·6 for osmophylic yeasts (*i.e.* sugar tolerant) to 0·8 for many moulds and 0·9 for most bacteria. Understanding of these factors determines not only conditions of harvesting and storage but also control of many dehydration operations. This method of preservation is used to a considerable extent for drying combine harvested grain as well as herbs, milk, eggs and soup mixes for human consumption, and is used on a very large scale for animal feeding stuffs. Quite often, residues from biological processes, for example sugar beet cossettes and distillers slops, are dried for blending into cattle cake.

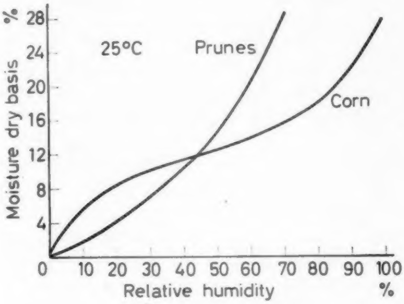

Figure 1

The choice of dehydration equipment is a reasoned compromise bearing in mind questions of capital cost, thermal efficiency, product damage from heat, oxidation or contamination and the physical nature of the material. Thus in the case of thermolabile solutions or suspensions, including milk, they may be concentrated first in a multiple effect vacuum evaporator and finally dried on either a roller drum or spray unit.

In a limited number of cases, it is possible to remove a significant proportion of the original water by freezing it out without incurring too high a loss by inclusion of the concentrate in the ice crystal*. This method is particularly applicable to fruit juices since their full flavour and aroma can be retained better than by most other processes and it is also used to increase the strength of wines.

Solid materials can be dealt with in numerous ways. The simplest and cheapest installations are driers using direct flue gas as the drying medium, and by careful combustion of a selected low sulphur low arsenic oil or coal, very satisfactory animal feeding stuff quality can be obtained. A limited level of sulphur, absorbed as sulphur dioxide, is in fact beneficial as a preservative. Such equipment, however, is not suitable for more refined products, and a range of tray and belt driers are available of different capacities and complexity, using steam heated air at atmospheric pressure.

* See 'Freezing, Freeze-drying and Freeze-concentration of Foodstuffs' by R. GANE (*Research* (1960) XIII, 207).

For the very highest product quality, vacuum driers or even freeze drying or lyophilization units can be considered. These latter operate at below freezing point and at such a low pressure that the mean free path of water vapour molecules is of the same order as the distance between the subliming surface and the very cold condenser. Under these conditions, molecular sublimation occurs at a slow but still useful rate. Such equipment is necessarily expensive to build and operate and so its use is restricted to materials of high market value and delicate constitution.

Uses of Radiation

In many cases, very prolonged storage of food-stuffs is not needed so much as some extension of shelf life to simplify transport and marketing, without incurring the high cost associated with deep freezing and canning. Great expectations were centred on the use of radiations, particularly ultra violet light and later gamma rays from radioactive cobalt or caesium; u.v. had for long been known as the major factor in the bactericidal value of sunlight and some success has in fact been achieved in sterilizing air and thin films of liquid. Its penetration is however too low for other applications, and when used at high dosage, there is a marked tendency to give flavour/odour spoilage before satisfactory sterilization is achieved.

With the advent and availability of radioactive elements and particle accelerators, a large amount of research has been carried out on their suitability for food sterilization*, but again the general result has been to find product damage before full destruction of the more resistant forms of spoilage organism. However, low level and carefully applied doses can often usefully extend the shelf life of foods without serious quality effects. Tests are continuing as there is a possibility that when eventually bacterial growth restarts it may be of abnormal type—either a different balance of flora or even of pathogenic mutations. A particularly interesting use is that when applied to grain, all weevils are sexually sterilized but not necessarily killed so that infestation cannot develop.

Bactericidal Solutions

Another approach has been that of applying dilute solutions of selected broad spectrum antibiotics

* See 'Processing by Irradiation—11—Application to Food Preservation' by LEY and HICKMAN (*Research* (1960) XIII, 193).

to fish, meat and poultry and thus reduce surface contamination. Under scientific control, results are most encouraging but it is important that the antibiotic used is heat-labile so that it is completely destroyed on cooking.

Brining and Smoking

Returning to more traditional methods, the same concept of water activity can be applied to preserving methods as divergent as jam making and kippering, although nutritional and osmotic requirements of micro-organisms are also important in these cases. When any solute is dissolved in water, it depresses the water activity; thus 1 mole concentration of a non-ionizing solute reduces activity to about 0·98, but this relationship is only linear at low concentrations. Also, of course, the high affinity of proteins and polysaccharides for water is a supplementary effect. A combination of these factors explains why it is necessary to have about 65 per cent sugar concentration in jam to prevent mould and yeast growth, but even so, a high degree of sterility is also desirable as some yeasts can exist even at these high sugar levels.

Brining and subsequent smoking of kippers, bacon, ham and some continental sausages depress microbial life by several mechanisms. The internal flesh of all healthy animals is usually fairly sterile, but subject to enzymic spoilage and the treatment is mainly directed at controlling external contamination. Brine is applied to give high surface absorption of salt, but with rather less inside, and this suppresses bacterial activity except for a few 'halophylic' types. The following smoking and partial dehydration then concentrates this salt and also adds various phenolic and tar-like compounds which are themselves bacteriostatic and these combined multiple actions, particularly if carried out to traditional intensities, greatly extend the storage life of these foods. Present day preference for milder cures and the emphasis on speed and reduced cost of processing are now tending to reduce these effects, but unless carried to a point of markedly reducing quality, this should not be serious if advantage is taken of modern sterility techniques, refrigerated storage and transport speed.

The Dairy Industry

Before the second world war, it was estimated that over 50 per cent of cattle in some areas were suffering from active bovine tuberculosis, and while this did not necessarily endanger the milk quality, sometimes the udders were affected, and the milk then contained live bacteria. Such milk was known to be a prime cause of human tuberculosis particularly affecting the lymph glands and bones of children. Steady and progressive pressure and education by the government has now almost overcome this and associated dangers to health and at the same time has brought about higher milk yields for the farmer. Although there have been criticisms, we as a nation can now take great pride in our milk farming and dairy industry.

The interest of biochemical engineering should really start at the cow and include the design of all equipment, its sterilization and all production methods from the udder to the consumer's doorstep. Milk as it is drawn from the ideal healthy cow should be practically sterile, but it is one of the richest and most balanced of all natural foods, not only for multicellular organisms such as man, but also for an enormous range of micro-organisms—both harmless and pathogenic. Even with modern milk byre equipment and techniques, practical considerations inevitably allow some bacterial and other contamination, and the whole emphasis of milk handling must be directed towards keeping this low and preventing its development. And as a final precaution, nearly all milk is now pasteurized under closely controlled conditions of temperature and time.

Great strides have been made in designing continuous pasteurizing equipment for the milk handling trade, mainly using HTST (High Temperature Short Time) conditions followed by rapid cooling

Figure 2. HTST pasteurizing plant. (Courtesy Express Dairy)

before filling into bottles just emerging from the continuous bottle washing and sterilizing machine. A high degree of standardization of plant has been achieved based on dismountable pipelines and regenerative heat exchangers of openable type. These may not however, represent the final scheme, as firstly plant sanitation is most labour consuming and secondly it is difficult to design such equipment that it can be completely sterilized at the requisite 120°C : 15 lb/in.^{2} : 15 mins to destroy even spores of thermophylic organisms. A unit has in fact been designed in Sweden based on a completely enclosed stainless steel system, cleaned by circulating detergents followed by strong nitric acid. This has much to commend it, as it can be made almost automatic and should remain free of bacteria as well as 'milk stone' deposits.

Ice Cream Manufacture

About the same time as legislation was being enforced for milk handling, new regulations came in for ice cream. These insisted similarly on pasteurization and final bacteriological standards, but also set minimum limits for fat and milk solids content, with the aim of ensuring a high nutritive value. The levels chosen were near those for 'American style' ice cream, the smooth rich type previously made only by the large scale manufacturers, which can be stored for several weeks at about −20°C. Many people regret this legal death blow to the old 'Hokey-Pokey', which was little more than frozen custard, but if hygienically produced is a pleasant variation capable of bringing back nostalgic memories.

This legislation forced small makers to remodel their formulae and to install new plant, and some very pretty 100 to 200 gallon installations were put in. These suffered from the same inherent disadvantages as milk plants and the control of thermophylic contamination remains quite a problem, particularly as this type of organism can be introduced on some of the usual ingredients.

Meanwhile the larger manufacturers were designing semi-continuous processes and this posed some very interesting biochemical engineering problems. The actual freezing is usually carried out in two stages, the first from say storage temperature of 6°C down to −4°C, using a rotary doctor blade inside a narrow cylinder and surrounded with direct expansion ammonia. At this temperature, only about 20 per cent of the water is frozen into minute ice nuclei and the product is plastic but capable of retaining an extruded shape. The resultant strip can then be cut into final size portions onto a conveyor belt and passed into a blast tunnel at −40°C or lower. One of the particular problems of this stage is that ice cream is a poor thermal conductor as it contains about 35 per cent of finely dispersed air (as 'over-run'), but freezing time cannot be too prolonged as it leads to a coarse ice crystal structure. Another adverse factor is that water vapour evaporates from the ice cream and is

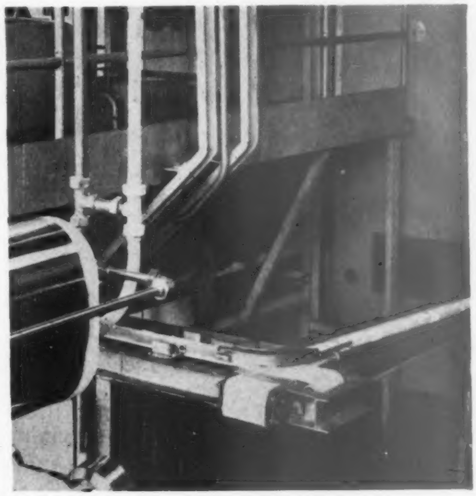

Figure 3. Freezing of ice cream. The semi-frozen mix is extruded onto a stainless steel belt which conveys it through a blast tunnel for rapid hardening. (By courtesy of T. Wall & Sons Ltd and Firth-Vickers Stainless Steels Ltd)

also introduced by the surrounding air and builds up as ice on the refrigeration coils, so reducing the effective heat transfer. As is usual in this type of problem, a compromise between conflicting factors has to be adopted, with a somewhat extravagant use of refrigeration.

From these tunnel freezers, the blocks are fed directly to wrapping machines and into cold storage. As with the milk industry, ice cream manufacture is at a most interesting and advanced stage but one feels that considerable development is still possible, towards greater automation, simpler plant sterilization and more positive quality control.

Other Dairy Products

Milk is essentially a moderately stable oil-in-water emulsion, the oil consisting of a complex blend of saturated and unsaturated triglycerides with traces of other lipids and oil soluble vitamins, and the aqueous phase containing mixed soluble proteins,

which act as emulsifying agents, plus lactose sugar, soluble salts and the water soluble vitamins. Typical average analyses from five breeds of cattle are shown in *Table 1*.

Table 1. Analysis of milk from five breeds of cows

	Guernsey	*Jersey*	*Ayrshire*	*Friesian*	*Shorthorn*
Water	85·1	85·3	86·9	87·5	87·4
Total solids	14·9	14·7	13·1	12·5	12·6
Fat	5·2	5·2	4·1	3·6	3·6
Protein	4·0	3·9	3·6	3·4	3·3
Lactose	4·9	4·9	4·7	4·9	4·9
Ash	0·7	0·7	0·7	0·7	0·7

You will probably feel it worth while to pay the small extra premium for ' Channel Island ' milk on these figures.

Cream

Standing or better still, centrifuging, concentrates most of the fat into a cream layer, which can contain over 50 per cent fat and still remain an oil-in-water emulsion, but with a tendency for the oil globules to coalesce. This can be sold as it is in legally defined grades, or it can be heated to coagulate the protein, so thickening the cream to ' scalded ' form. Alternately, and perhaps the most pleasant form of all, this warming can be extended and the surface allowed to form a crust, which can be repeatedly worked in, to give the granules of clotted cream.

Butter

Separated pasteurized cream is the starting point for butter manufacture, which consists in making the emulsion invert to a water-in-oil type, the residual emulsifying agents retaining some buttermilk in fine dispersion—with a legal moisture limit of 16 per cent. Freshly separated cream does not easily invert, but can be made to do so at cool temperatures, to give a sweet and rather underflavoured butter. Particularly in this case, foam is formed and appears to aid the inversion by increasing the concentration of ingredients at the air–liquid interface.

Normally, bacterial ' ripening ' is allowed to take place for 1 to 4 days, by making use of natural contaminants or by deliberately adding a ' starter '. This is usually a mixed culture of *Streptococci* and other micro-organisms selected to produce both lactic acid and also flavouring components of the diacetyl and acetoin type and to bring about some denaturation of the protein. After this ripening process, churning quite rapidly causes grains of butter to form, which coalesce into lumps. The buttermilk is then drawn off, the butter washed with chilled water, salted and kneaded into the final pack.

Equipment and technical control have come a long way from uncontrolled ripening and the old wooden farmhouse churn, and the factory product is altogether more uniform and of longer shelf life, although perhaps lacking the rich flavour the best of farm butter achieves.

Cheese

The main protein of milk is casein with an isoelectric point at pH 4·6 and the manufacture of the enormous number of cheese varieties centres round the control of this protein. The starting point may be cream, full cream or skim milk and quite often is from goats or sheep as well as cows. Under factory conditions, it is always pasteurized before use. Actual operating conditions vary as between types of final product, which range from very dry (*i.e.* about 20 per cent moisture) Parmesan to very soft cheeses as high as 60 per cent water, with all the intermediate varieties such as Cheddar, Stilton and Camembert. Some cheeses are inoculated during manufacture with various moulds, *e.g. Penicillium roquefortii* which gives a green colour and full flavour.

A typical sequence is to inoculate the cooled pasteurized milk with a blend of micro-organisms which give a suitable level of acidity within a few days but also continue to work during the months of maturation to develop the correct flavour and also to modify the casein. Sometimes this is required of rubbery consistency as in Emmenthal or in a crumbly form as in Cheshire; also it may be necessary for gas bubbles to form to give holes as in Gruyère. The choice of initial culture is obviously of over-riding importance.

To return to the making process. When the required level of acidity is reached, rennin (an enzyme extracted from calves stomachs) is added to bring about a rapid coagulation of the protein. This forms a curd which occludes an appreciable proportion of the other milk components. By very carefully controlled mechanical ' cutting ', this is made to throw down the whey and to gather in a fairly firm mass. Residual whey must be hastened out of this by stacking operations and when it is dry enough, it is milled and salted prior to wrapping, pressing and careful ripening over several months.

There has been considerable mechanization of cheese manufacture, but a great deal of hand labour is still used, partly because it is important to control the curd texture by careful treatment. Further automatic handling will undoubtedly be developed in cheese making as in other food industries and it is hoped this will be applied by biochemical engineers unwilling to sacrifice traditional quality for speed and convenience.

RADIOLOGICAL DECONTAMINATION

Theoretical and Practical Aspects

D. G. STEVENSON

Atomic Weapons Research Establishment, Aldermaston

The factors involved in the adsorption of radio isotopes on non-metallic surfaces include ion exchange, physical adsorption and direct penetration, although in many cases ' surface films ' act as barriers. On metallic surfaces contaminants appear to be bound by adsorption on oxide films or by exchange with the metal itself. The method of removal must be related to the mechanism by which the contaminant is held, but may be broadly classified as detergency, ion displacement and surface removal.

RADIOACTIVE contamination tends to be somewhat of a mystery to the layman especially in that it cannot be seen or detected other than by a suitable instrument. However a close examination reveals a problem which may be defined in normal physical and chemical terms, and which will respond to scientific investigation. Chemically, one is dealing with a minute quantity of any one or more of the known elements, and their behaviour will be identical with that of their stable counterparts, the only difference being that the hazardous material is capable of emitting ionizing radiation.

The particular feature of most radioactive contamination is the extremely small weight associated with permissible levels of contamination. An isotope of half life equal to one year will have a specific activity of $8{\cdot}1 \times 10^{17}$ disintegrations/min/g atom. Permissible levels amount to 400 disintegrations/min/cm^2 for most isotopes, hence the quantities involved are very small indeed, and are detectable only with instruments which are sensitive to the radiation.

The approach towards handling radioactive material, apart from direct shielding, is to confine the material and handle it in such a way that the spread of radioactive dust or liquid is kept to a minimum. Hence fume cupboards with filtered extraction and glove boxes are used extensively. Where larger areas of loose contamination have to be entered, suitable protective clothing with means for breathing uncontaminated air are necessary. Any surface which has come into contact with radioactive material, or even in contact with another contaminated surface is potentially contaminated; thus decontamination is an essential operation in the running of any plant or laboratory handling radioactive material. Maintenance operations are necessary on radioactive plant, and also with the possibility of accidents, quick and efficient methods of cleaning must be available.

In the early days of the atomic energy industry when little was known about the science of decontamination, many unnecessarily drastic treatments were employed and frequently items being treated were rendered useless in the process. Nowadays with more refined techniques and reagents damage is less, and the efficiency far higher.

Mechanisms of Contamination and Decontamination

Ion Exchange

Ion exchange probably constitutes the most important single adsorption process in surface contamination by radio isotopes[1]. All organic surfaces such as paints, plastics and floor coverings, and also vitreous surfaces such as glass and porcelain, possess surface acid groups, partly by virtue of their inherent nature and partly by surface oxidation. Although the adsorption capacity is small compared with conventional ion exchange resins, this capacity is nevertheless more than adequate for the retention of high levels of radio isotope contamination of high specific activity. As an example, cotton which is used extensively for protective clothing, has, when purified, an ion exchange capacity of 10 μ equiv./g^2, the pK value of the acid groups being 3·3.

At pH values above about 2 surface acid groups ionize and behave as weak low capacity ion exchangers. Anions are repelled from such surfaces and little adsorption is detectable, providing such anions remain ionized and do not react chemically with the surface. Cations on the other hand possess a direct affinity for such surfaces and the polyvalent cations under conditions of low ionic concentration are adsorbed almost quantitatively. The behaviour is identical to that on any comparable ion exchange resin.

Contaminant ions adsorbed on to a surface may to some extent be displaced by high concentrations of sodium ion (*Figure 2*) but the efficiency is poor.

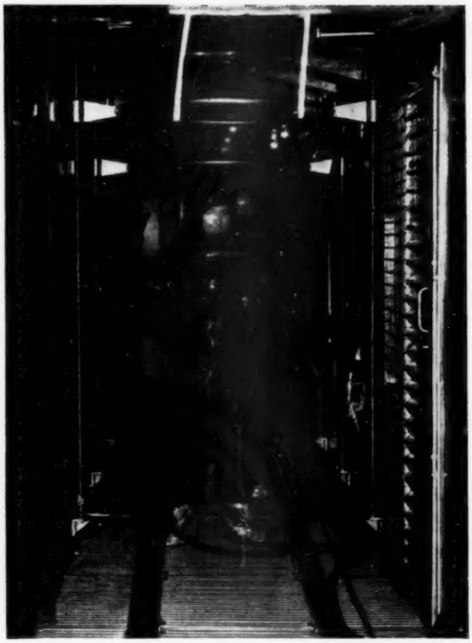

Figure 1. Operators in pressurized suits being sprayed with decontaminant from ring jets on leaving a highly contaminated area

The high pK value enables moderately dilute acid solutions to have some effect as illustrated in *Figure 3*; however to remove polyvalent ions adequately, relatively strong acid solutions are required and degradation of many surfaces would be expected.

A far milder but nevertheless effective treatment is the use of polyvalent ions such as ferric or aluminium to displace the contaminant. For example in one particular experiment residual cerium was reduced to 1·5 per cent on treating with 1·2M aluminium sulphate, whereas under identical conditions the residue in 1·2M sodium acetate was 25–30 per cent.

In practice, however, purely 'mass action' methods are seldom attractive compared with the use of complexing agents. In recent years a number of useful reagents have become available on a commercial scale, in particular ethylene diamine tetra acetic acid (E.D.T.A.) which forms extremely stable complexes with many contaminant ions.

In order that a contaminant may be removed from a surface it is necessary to form a water soluble anionic complex. Thus ammonia triacetic acid (A.T.A.) is suitable for divalent ions, but E.D.T.A. is necessary for trivalent ions. Such anionic complexes will be repelled from the surface as a result of the Donnan Equilibrium. Neutral complexes such as Ce^{III} (A.T.A.) or Pu^{IV} (E.D.T.A.) will be less effective (*Figure 4*). By virtue of the above repulsion and also of the great stability of the iminodiacetic acid type complexes fairly dilute solutions suffice to give good results, and contrary to 'mass action' methods, protection against redeposition of the contaminant persists during the dilution which accompanies rinsing.

Reagents such as E.D.T.A. show a great sensitivity towards variations in the pH value, and some workers have been misled by studies at high pH values. The rate of decontamination will be a function of the concentration of the complexing reagent within the surface. This in turn will be governed by the Donnan Equilibrium in relation to the external ionic concentration and the degree of ionization of the reagent. E.D.T.A. being tetrabasic has four pK values (*viz.* 2·00, 2·67, 6·16 and 10·26)[3]. A simple calculation on the Donnan theory provides figures similar to those given in *Table 1*, which are based on an internal carboxyl normality of 0·1N (10 μ equiv./g carboxyl content, and assuming 100 mg solvent water/g in cotton).

Table 1. Internal concentration of E.D.T.A. in cotton (calculated)

Degree of ionization of E.D.T.A.	*1*	*2*	*3*	*4*
External 1	1			
Ionic 10^{-1}	0·06			
Activity 10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
10^{-3}	10^{-5}	10^{-7}	10^{-9}	10^{-11}
10^{-4}	10^{-7}	10^{-10}	10^{-13}	10^{-16}

From this one may expect the decontamination rate to rise rapidly with total ionic concentration and fall off steeply with increasing pH value. The latter effect is illustrated in *Figure 5*, in which non-equilibrium conditions were used.

Two further complications are, firstly, at low pH values the complex breaks down due to reversion of the reagent to the un-ionized acid form, and ultimately to the cationic ammonium form. Simultaneously however the hydrogen ion tends to displace the contaminant (*cf. Figure 3*) with the result that a hump appears in some curves (*Figures 4* and

5). Secondly at high pH values the complex is hydrolysed[4] due to the very low solubility product of many heavy metal hydroxides.

From the practical viewpoint therefore a solution of E.D.T.A. together with a suitable buffer of fairly low pH value and a wetting agent provides a useful and versatile composition for removing contamination bound by ion exchange forces[5]. A citrate buffer in particular has been found useful and there appears to be a synergism between this and E.D.T.A. Elevated temperatures are also desirable since the activation energy appears to be around 10–15 kcal/mole.

Physical Adsorption

Compared with ion exchange physical adsorption is of relatively minor consequence. The chief example is that whereby strong solutions of salts and alkaline solutions assist the displacement of anionic contaminants from surfaces with no chemical anion exchanging properties. Anionic detergents are also effective in this respect, as may be expected from their surface activity and inherent tendency to be adsorbed at interfaces with consequent rise in negative zeta potential[6]. The addition of an anionic detergent assists the removal of anionic E.D.T.A. complexes.

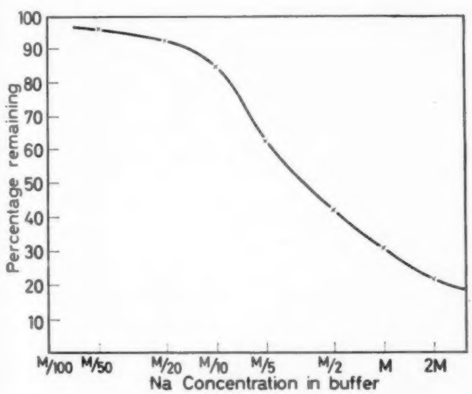

Figure 2. Residual cerium-144 on cotton after treatment with sodium acetate at pH 5, for 24 h at 25°C

Penetration of Organic Materials

The high affinity between carboxyl groups and polyvalent metal ions enables such contaminants to be retained at the surface and little penetration of micropores of organic surfaces can occur. Under acidic, or strong ionic conditions, however, ionization of the surface acid groups is suppressed and Donnan effects swamped. As a result both anions and cations will be able to diffuse further into the surface and removal will become more difficult.

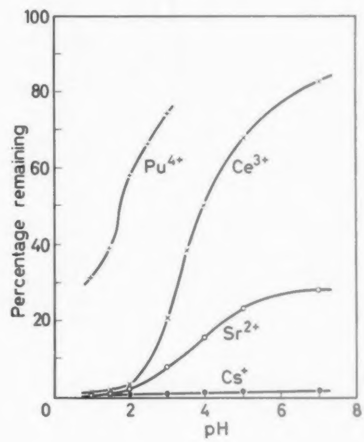

Figure 3. Residual cationic contamination on cotton after treatment with a range of sodium acetate/hydrochloric acid buffer solutions. (N/5 sodium acetate, 24 h, 25°C)

A rather worse problem arises where the contaminant is able to dissolve in the organic phase. Many inorganic compounds are soluble in organic solvents, *e.g.* halogens, many acids, heavy metal salts, *etc.* In this respect one may regard a polymer as a gelled high molecular weight solvent. The partition of inorganic compounds between aqueous and organic phases will be governed by the nature of the two phases, and also the presence of other components which can form complexes with the solute. This field has received intensive study both in relation to analytical chemistry and more recently in industrial chemistry, as for example in the solvent extraction and separation of fissile materials and fission products in reactor fuel elements[7].

Many curing agents, plasticizers and other ingredients of technical polymeric compounds tend to form oil soluble complexes with heavy metals under acid conditions. One may compare the kerosene–tributyl phosphate system used in some extraction processes with phosphate plasticized polyvinyl chloride (p.v.c.) A considerable amount

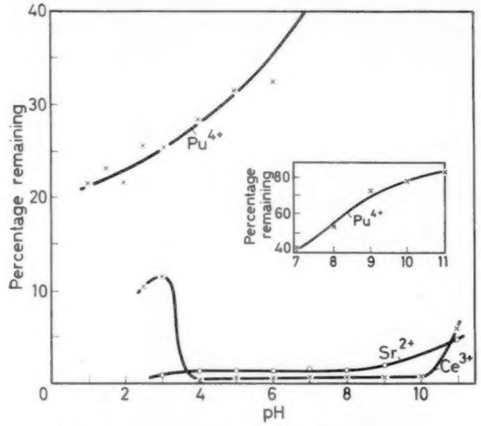

Figure 4. Residual cationic contamination on cotton after treatment with buffered solutions of ethylene diamine tetra acetic acid (0·1 per cent E.D.T.A., Na ion approx M/20, 25h, 25°C)

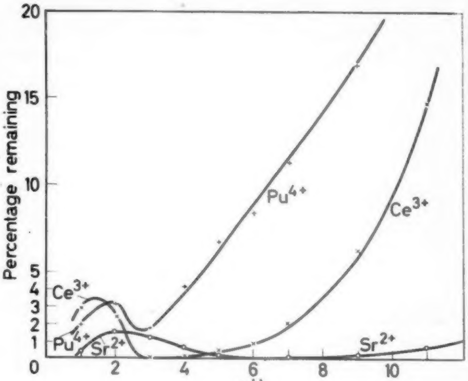

Figure 5. Residual cationic contamination on cotton in a practical formulation (0·1 per cent E.D.T.A., 0·2 per cent citric acid, 0·03 per cent alkyl sulphate, sodium hydroxide as necessary, 15 mins, 70°C)

of data is available relating to the extraction of metals such as uranium, plutonium and certain fission product elements. In general the partition coefficient with respect to the organic phase[8] rises with the hydrogen ion concentration to a peak under strong acid conditions. The addition of salts, *e.g.* sodium nitrate to nitric acid produces an even stronger extraction into the organic phase. This behaviour is reflected closely by phosphate plasticized p.v.c. (*Figure 6*).

The effect of added salt in this context is in direct contrast to the ion exchange system where added salt discourages absorption, by a mass action effect. HEALY and MCKAY[9] have concluded that tributyl phosphate forms complexes or solvates with the un-ionized heavy metal nitrate, this complex being soluble in the organic phase. The higher phosphates such as tritolyl phosphate frequently used in plasticized p.v.c. appear to behave in a similar manner.

Many amino compounds also form solvent soluble complexes with heavy metal salts and polymers containing amino nitrogen, *e.g.* amine and polyamide cured epoxy resins, polyamide plastics *etc.* tend to resist decontamination after contact with acidic radioactive solutions.

A further example of penetration is provided by radio-iodine. Under acid conditions there is a tendency for iodides to oxidize to elementary iodine, as is demonstrated by the colour of solutions of hydriodic acid. Elementary iodine is soluble in most organic media. *Figure 7* illustrates this effect as it applies to cotton contaminated over a range of pH values.

In general where the contaminant has penetrated into a material little can be done to remove it. The situation will be alleviated to some extent by prompt cleaning of the surface before much penetration has occurred, but if some time has elapsed the rate of outward diffusion will be too low to be of any practical value. The ultimate remedy is the avoidance of surfaces with a high aqueous absorption containing ingredients liable to form complexes with radioactive contaminants.

Metal Surfaces

Much of the basic information on the behaviour of metal surfaces with respect to contaminants has been provided by electrochemists, and much of the relevant literature has been reviewed by KING[10].

Surface oxide films govern the behaviour of most practical metals. In some cases this film is protective; in other cases the underlying metal is able to participate in an independent absorption process alongside the oxide film. Workers in the U.S.A.[11,12] using cobalt-60 have examined the adsorption on a number of metals. Some oxide films such as copper are particularly susceptible to contamination whereas others, *e.g.* steel and aluminium, adsorb far less. The nature of the adsorption process is not clearly defined at present, although some form of exchange or combination with the oxide film seems likely.

In the absence of oxide films, or where they are not protective the contaminant ion will exchange with the metal surface. As early as 1929 von Hevesy and Blitz[13] used natural ThB (Lead–210) as a tracer to study lead–lead ion exchange, and concluded that 1000 surface atomic layers were involved in the process. More recently King and Simonsen[14] have shown the silver/0·5N silver nitrate system to possess an exchange rate equivalent to 4×10^{-9} A/cm^2, involving 35 to 50 atomic layers of the surface. It has also been found that with alkali metal amalgams where the surface layer mixes with the bulk metal, the exchange current corresponds to over 1 A/cm^2.

In addition to kinetic exchange between a metal and its own ions normal electrochemical exchange between less noble metals and solutions of more noble ions will occur, as on the macroscopic scale, *e.g.* iron will absorb copper-64 from solution. Conversely from the kinetic theory one would expect less noble ions to exchange to a small extent with more noble metals. This is particularly likely where the two are close together in the electromotive series. Such exchanges do not appear to have been verified[10], although conclusive proof would not be an easy matter.

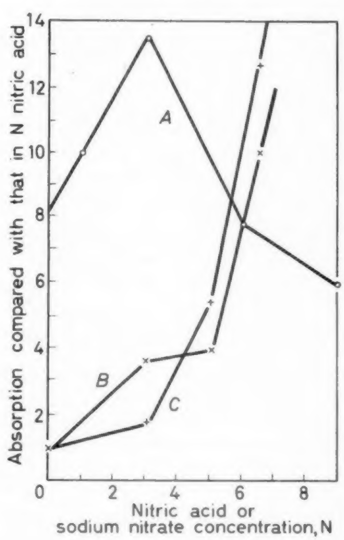

Figure 6. Absorption of contaminants by tributyl phosphate plasticized polyvinyl chloride under acid conditions

A. Relative absorption of cerium over a range of acid concentrations (24 h, 25°C)

B and C. Relative absorption of cerium–144 and plutonium–239 in N nitric acid with added sodium nitrate (24 h, 25°C)

In addition to the above exchange reactions there is considerable evidence that local electrochemical action, similar to that which is responsible for much metallic corrosion, is a major factor in the adsorption of ions at a metal surface. Factors such as contact between dissimilar metals, impurities in the surface, variations in ionic or oxygen content of solutions in contact with the metal *etc.* all cause local electrolytic cells encouraging dissolution of metal at anodic areas and deposition of metal ions at cathodic areas. Workers[11,12] using cobalt-60 have demonstrated this effect by immersing bi-metallic couples in solutions, and subsequently obtaining auto-radiographs. These workers considered local electrochemical action to be the most important process in the absorption of cobalt-60 by metals.

To turn to anionic contaminants, Hackerman[15] and others have shown that weak chemisorption occurs with chromate and sulphate ions on metal surfaces. Other ions are able to compete and alkalis, or strong solutions generally, assist decontamination. The metal surface thus acts as a low capacity anion exchanger.

From the foregoing it will be realized that in order to remove the contaminant a few atomic layers of the surface must also be dissolved away. The reagent chosen must be able to do this without etching or pitting which would render the surface more liable to contamination subsequently. Inhibitors as used in metal pickling are useful additives where the contaminant is bound to the oxide, but where exchange with the metal has occurred such additives are a hindrance. Steps must also be taken to avoid readsorption of the contaminant on newly exposed metal surfaces. To this end it is necessary to have turbulent conditions and a continuous flow or reagent is desirable. Reagents with an inherent complexing power also assist in this direction but again such reagents may become exhausted by ions from the metal surface unless constant agitation is applied.

Detergency

Conventional detergency[16] is concerned for the most part with oily and greasy matter and solid particulate dirt. Apart from the limited field of carbon-14 work the oily and greasy aspect is not a primary concern in decontamination. Radioactive material is frequently present in a solid particulate form but the removal of such material involves factors

similar to those which operate in non-radioactive detergency.

However, a number of secondary effects arise which bring conventional detergency and decontamination much closer together and enable similar compositions often to suffice for both duties. Under many practical conditions the contaminant is adsorbed on a fairly easily removable surface film and not on the true surface itself. For example all surfaces exposed to the normal atmosphere, particularly in industrial areas, adsorb at least a monolayer of greasy matter within a very short time[17] (as short as one hour). Also all organic surfaces are subject to oxidative degradation, particularly in the presence of ultraviolet light. Such films provide a barrier which will modify the normal contamination -decontamination processes already discussed. To decontaminate, one may either remove the contaminant from the surface film (*e.g.* with a mildly acidic complexing agent solution) or one may remove the film itself together with adherent contaminant (*e.g.* with an alkaline detergent solution). It is more satisfactory to remove the surface film together with any loose dusty contamination before using the more expensive complexing reagent on stubborn residues which are bound to the true surface.

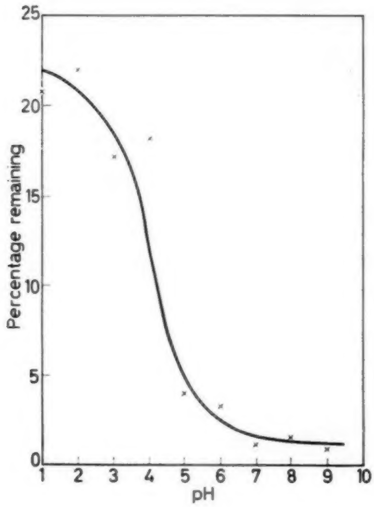

Figure 7. Residual iodine-131 on cotton washed in sodium carbonate buffer (15 mins, 70°C) where the contaminant has been applied in buffer solutions of varying pH value

The requirements for a detergent for radioactive work are in the main similar to one for non-active cleaning. ' Built ' detergent compositions containing ingredients such as sodium tripolyphosphate are far more effective than simple surface active agents. Furthermore, particularly in the case of soap-based compositions, an optimum pH value exists, necessitating buffering ingredients. E.D.T.A. is a valuable addition as it prevents contamination in solution from being readsorbed onto freshly cleaned surfaces. In this way the apparent efficiency is improved and cross contamination minimized. Very small amounts of E.D.T.A. are currently used as bleach stabilizers in commercial detergent compositions[18], but rather more is necessary for the present purpose. Many other ingredients of commercial formulations have no effect in decontamination, *e.g.* fluorescent brightening agents, foam stabilizers, bleaches *etc.*, while some materials may be deleterious, *e.g.* certain blue dyes and corrosion inhibitors.

Practical Considerations

Reagents for decontamination may be divided into classes depending upon their mode of action and severity:

(*a*) *Detergents* (mildly alkaline)—for loose contamination, ' surface films ' *etc.*

(*b*) *Complexing compositions* (mildly acidic)—for ion exchanged contamination, metals *etc.*

(*c*) *Dilute acids and mixtures, e.g.* 1 per cent sulphuric acid—for more resistant contamination.

(*d*) *Stronger chemical treatment, e.g.* nitric–fluoride mixtures—for very resistant contamination.

In addition scouring preparations may be prepared by the incorporation of abrasives *etc.* into the milder reagents. It is of course preferable to use the mildest, most dilute reagent which will give the required degree of cleansing, to achieve the minimum damage to the surface, economy of materials and easy effluent disposal. The liquor used in any bath treatment will usually be unacceptable on contamination grounds long before chemical exhaustion has occurred.

Most decontaminants are of general application regardless of the isotopes concerned. The majority being metal ions have a sufficiently common behaviour for this to be so. Nevertheless certain specific treatments are available, *e.g.* fluorides catalyse the cleaning of these metals[5] which have soluble fluorides but hinder the action on other metals.

Since a high efficiency is usually required in radioactive work dilution factors often present a practical restriction, and must be taken into account. In this respect it is more satisfactory to use a shower cabinet with continuous flow than to immerse an item in a tankful of liquid. It is unfortunate that damp cloths are necessary in cleaning walls and ceilings in order to avoid splashing of contaminated washings. The rinsing efficiency of this method is very low and repeated treatment and frequent replacement of rags and mops is necessary if cross contamination is to be avoided. On large scale operations such as the recovery of the Canadian reactor[19] very large quantities of such items may be used.

Some of these difficulties may be overcome by thickening the reagent with, say, sodium alginate, which will reduce the risk of drips and enable the reagent to be kept in contact with walls *etc*. Also the addition of a pigment or dyestuff will ensure full coverage of the surface by the reagent as it is applied and likewise on rinsing or wiping off. One of the most promising recent developments in this field is the use of natural rubber latex[20]. This may be brushed or sprayed onto a dusty contaminated surface, allowed to dry and subsequently pulled off in large elastic sheets, which remove most of the loose contamination on the surface. To go a stage further a suitable detergent may be incorporated and the mixture scrubbed onto the surface. Instead of rinsing however a further coat of latex is applied and the mixture allowed to dry, subsequently to be peeled off. This avoids the free use of water in rinsing and the need for large quantities of rags *etc*.

As a last resort if all the more refined techniques fail it is necessary to remove the surface. Brick and concrete are almost impossible to clean and either chemical or mechanical surface removal must be used. Wet grit blasting is widely applicable, but in recent years this has been developed into a precision method which can give controlled removal of the surface of metals and a good surface finish.

Conclusions

Decontamination tends to be regarded as a somewhat unglamourous sequal to many more interesting advances in the atomic energy field. However efficient cleaning is now a necessity both from the economic point of view, in reducing the volume of contaminated waste for disposal, in avoiding replacement costs; and also from the aspect of health hazards.

As a result of systematic study the chemistry of the process is beginning to be understood and improved reagents, techniques and surfaces for radioactive areas are being developed. At present much must still be done by way of education to ensure that laboratories and plant are correctly designed and surfaces treated in such a way that decontamination is facilitated.

The aim of this work is to be in the position of having quick, cheap, safe and efficient methods of treating all practical cases of contamination, and to know how to formulate and specify good decontaminants and surface finishes.

Figures 2-7 were originally published in Surface Phenomena in Chemistry and Biology[1] *and are reproduced by courtesy of Pergamon Press.*

References

1 STEVENSON, D. G. *Surface Phenomena in Chemistry and Biology*, (*eds* DANIELLI *et al.*) London: Pergamon Press, (1958) p. 140
2 SOOKNE, A. E. and HARRIS, M. *J. Res. Nat. Bur. Stand.* (1940) **25**, 47; (1941) **26**, 265
3 MARTELL, A. E. and CALVIN, M. *Chemistry of the Metal Chelate Compounds* New York: Prentice-Hall (1953)
4 JONES, S. S. and LONG, F. A. *J. phys. Chem.* (1952) **56**, 25
5 STEVENSON, D. G. *Brit. Pat. Appln 10212/58*
6 STANLEY, S. *J. phys. Chem.* (1954) **58**, 533
7 SPENCE, R. *J. Inst. Chem.* (1957) **81**, 357
8 FLETCHER, J. M. *Peaceful Uses of Atomic Energy* (1956) **IX**, p. 459, United Nations, Geneva
9 HEALY, T. V. and MCKAY, H. A. C. *Trans. Faraday Soc.* (1956) **52**, 633
10 KING, C. V. *Ann. N. Y. Acad. Sci.* (1954) **58**, 910
11 FOLEY, R. T., STARK, B. T. and GUARE, J. *J. electrochem. Soc.* (1956) **103**, 534
12 VON HEVESY, A. and BLITZ, M. *Z. phys. Chem.* (1929) **83**, 271
13 SIMNAD, M. T. and RUDER, R. C. *J. electrochem. Soc.* (1951) **98**, 301
14 KING, C. V. and SIMONSEN, A. H. *J. electrochem. Soc.* (1957) **104**, 194
15 HACKERMAN, N. and POWERS, R. A. *J. phys. Chem.* (1953) **57**, 139; HACKERMAN, J. and STEPHENS, S. J. *ibid* (1954) **58**, 904
16 LAWRENCE, A. S. C. *Nature, Lond.* (1959) **183**, 1491; STEVENSON, D. G. *J. Textile Inst.* (1953) **44**, T12; *The Mechanism of Detergent Action*, Ph.D. Thesis, University of London (1951); SCHWARTZ, A. M., PERRY, J. W. and BERCH, J. *Surface Active Agents and Detergents*, **I** and **II**, New York; Interscience 1949 1958
17 ADAM, N. K. *Physics and Chemistry of Surfaces* (3rd Edn) London: O.U.P. (1941) p. 174
18 HEDLEY, Messrs T. & Co. *Brit. Pat. 765,750* (1956)
19 HUGHES, E. O. and GREENWOOD, J. W. *Nucleonics* (1960) **18**, 76
20 GUNN, E. E. *Brit. Pat. Appln 17938/58*

PROPERTIES OF GRAPHITE

Part I—Preparation, Structure and Mechanical Properties

L. C. F. BLACKMAN

Department of Chemical Engineering, Imperial College of Science and Technology, London

In recent years there have been great advances in our knowledge of the properties of graphite and of its crystal compounds. In this, and in two subsequent articles which will appear in ***Research***, some of the important aspects of the subject are discussed. Special attention is paid to the influence of structural and chemical imperfections on the various properties of graphite.

GRAPHITE has been used for a great many years as a refractory material, as an electrical conductor and as a solid lubricant, but it is only comparatively recently that detailed studies have been made of its fundamental structural, chemical and physical properties. The increased attention paid to graphite during the past decade, as illustrated, for example, by the striking increase in the number of papers presented at the biennial conferences on carbon at Buffalo, New York, since their inception in 1953, can only partly be attributed to its current use in the nuclear power industry. New applications are being found which utilize its unique mechanical, thermal and electrical properties. Although our knowledge of certain aspects of graphite is now well advanced this highly anisotropic form of carbon still presents a challenge to chemists, physicists and engineers alike which cannot be ignored in the present surge of interest in solid materials.

Graphite exhibits many extreme properties as a result of its highly anisotropic crystal structure. For example, the very strong bonding within the carbon hexagon layers leads to its extremely high thermal conductivity in this direction and to its great thermal stability to temperatures approaching 4000°K. In contrast, the very weak bonding between the parallel layers results in it being one of the softest substances known. As a result of having an energy band structure in which at 0°K one full band is separated by a negligible energy gap from a second empty one, graphite has electronic properties intermediate between those of metals (partly filled conduction bands) and semi-conductors (two conduction bands separated by a finite energy gap).

On account of its marked layer structure most properties of graphite are anisotropic—many of them being extremely so. For example, the electrical resistivity in the direction perpendicular to the layers is about 10^3 to 10^5 times greater than that in the direction of the layers. From the chemical standpoint the layer structure allows graphite to form a wide range of crystal compounds by intercalation of various atoms or molecules. In these 'lamellar' compounds the carbon macromolecules act either as an acceptor or as a donor of electrons with respect to the intercalated species; this transfer of charge modifies the π-electron bands to the extent that in the direction of the layers the electrical resistivity of some of these compounds can exceed that of metallic nickel.

A major difficulty encountered in graphite research is that specimens of perfect graphite are extremely rare and very small in size. Much of our knowledge, therefore, is based on studies made on defective and often polycrystalline material and may be subject to rather serious errors. The present uncertainty in the precise value of the anisotropy of electrical resistivity mentioned above arises from this cause. The preparation of graphite single crystals of sufficient size to permit the precise determination of the anisotropic physical properties has not been achieved to date due to diverse technological difficulties. However, significant advance towards this goal can be expected in the near future.

The aim of this and the subsequent articles is to present a general account of most of the important aspects of graphite and of its crystal compounds. The influence of structural and chemical inperfections on the properties of graphite is stressed where appropriate. No mention is made, however, of the rather extensive and separate subject of the gas reactions of graphite[1,2].

Crystal Structure of Graphite

Diamond and graphite represent the extreme structures in which carbon can exist as a solid. In the isotropic diamond structure all bonds are equivalent being formed by overlap of sp^3 hybrid orbitals. The effective overlap leads to very strong bonds and hence to the fact that diamond is the hardest natural substance known. In the graphite structure, however, as in the case of aromatic compounds in general,

carbon utilizes only two of its three $2p$ orbitals (after the ground state

$$2s^2 2p^2 \longrightarrow 2s2p_x2p_y2p_z$$

the excited state) to form strong trigonal sp^2 type σ bonds between atoms within a plane. Additional in-plane bonding arises from lateral overlap of the remaining $2p_z$ orbitals. Although the double bond character in graphite is weaker than in simple aromatic molecules, *i.e.* the C—C bond length of 1·415 Å is longer than that in benzene (1·39 Å), the structure of ideal graphite approximates closely to a system of infinite layers of fuzed benzene rings. The individual layers of carbon hexagons are held parallel at a separation of 3·354 Å by weak van der Waals type forces. One consequence of the vastly different C—C distances between carbon atoms in the directions parallel and perpendicular to the layers is the highly anisotropic hardness of graphite. In the direction of the layers the hardness is close to that of diamond but in the perpendicular direction the hardness is very nearly the lowest known.

The Hexagonal Lattice

Following earlier x-ray studies of the structure of graphite BERNAL[3] in 1924 proposed the now accepted stable hexagonal lattice which is illustrated in *Figure 1.* The carbon hexagon layers form a stacking sequence (*ABAB*..) where one half of the carbon atoms in any one layer lie above the centre of the hexagons in the layer immediately below. The unit cell (space group $P6_3/mmc$) contains four atoms and has dimensions $a = 2{\cdot}456$ Å and $c = 6{\cdot}7076$ Å (twice the interlayer distance). These dimensions give a theoretical crystal density of 2·267 g/cm³.

The Rhombohedral Lattice

Although the predominant layer stacking in graphites of various origin is (*ABAB*..) in some cases a small percentage of the stacking is (*ABCABC*..) where only every fourth layer is in juxtaposition with respect to the *c*-axis. This modification, which corresponds with a rhombohedral unit cell, was proposed by LIPSON and STOKES[4] in 1942 to account for additional reflections found in the x-ray diffraction pattern. It is not usually present in synthetic graphite but is found in some natural specimens to the extent of 30 per cent[5]. It is metastable with respect to the hexagonal form, from which it may be produced by mechanical deformation[6,7] (unidirectional pressure plus shear—as in grinding), and is removed by heat treatment to around 1300°C or by boiling in acids. HAERING[8] has recently reported a preliminary analysis of the electronic band structure of rhombohedral graphite which suggests that a modification of electronic properties may be expected.

An orthorhombic structure for graphite has been proposed by LUKESH[9] to account for x-ray reflections which do not fit either the hexagonal or rhombohedral lattice, but this has not been established with any certainty.

Defect Structures in Graphite

The concept that graphite consists of infinite layers of carbon hexagons needs modification when reference is made to actual specimens found in practice. Various types of crystal defects may be present which can lead to a profound modification of chemical and physical properties. In a given specimen of graphite more than one type of defect is likely to be present but it is convenient to classify the defects as follows:

Edge Defects

If all carbon atoms in graphite are in sp^2 hybridization then those at the edge must either have one unpaired electron (free radical condition) or be bonded to foreign atoms or groups, such as —H, —OH, —C≡H *etc.* Alternatively the edge atoms could revert to the s^2p^2 divalent state and therefore become removed from conjugation with the π-electron system. Whatever the nature of the edge atoms the π-electron system will be influenced, either directly or indirectly, and this may have a significant effect on those properties that are sensitive to the π-electron distribution. The extent of such

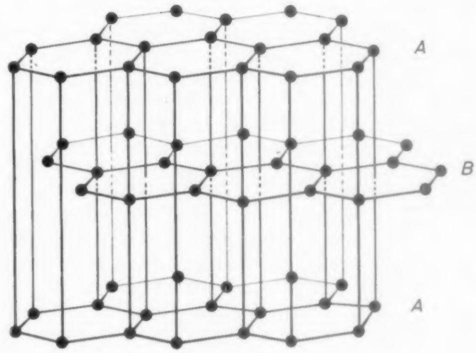

Figure 1. Structure of the hexagonal form of graphite

effects is obviously interrelated with the crystallite size since this determines the relative proportion of defective carbon atoms. An estimate of the crystallite size may be obtained from the sharpness of the x-ray reflections. Sharp ($hk0$) and ($00l$) reflections

indicate large extensions of the crystallites in directions of the *a*- and *c*-axes respectively. The use of X-ray diffraction to evaluate departures from ideality is, however, subject to the disadvantage that only statistical results are obtained and small amounts of non-ideal graphite can be obscured by the major proportion of ideal structure.

Turbostratic Structure

Whereas ideal graphite exhibits sharp three-dimensional (*hkl*) reflections, in many imperfect graphites these are diffuse or even missing. This arises from a loss of three-dimensional order through the random rotation of a certain proportion of layer planes perpendicular to the *c*-axis. BISCOE and WARREN[10] termed such an arrangement of misoriented layers ' turbostratic '.

From an analysis of many non-graphitic and graphitic carbons FRANKLIN[11] concluded that two basic interlayer spacings exist for a system of parallel carbon macromolecules whose layer diameter exceeds about 100 Å; these are 3·44 Å between adjacent misoriented layers and 3·354 Å between correctly oriented layers. On this model the measured ' apparent ' interlayer spacing of a given specimen of graphite is the mean of the proportion p of misoriented layers and $(1-p)$ of oriented layers. The relation between the measured interlayer spacing d and the factor p, which can be determined from a detailed study of the line shapes of the (114) and (116) reflections, is given by the empirical equation[12].

$$d = 3{\cdot}44 - 0{\cdot}086(1-p) - 0{\cdot}064p(1-p)$$

With increasing disorder of the layer stacking from ideal graphite p varies from 0 to 1. For a typical reactor grade graphite of mean interlayer spacing 3·36 Å the value of p is 0·17 and therefore, on average, one layer in six is misoriented.

Vacancy and Bond Defects

The pronounced rise in the specific heat of graphite above about 3200°C[13] may in part be due to the formation of vacancies in the carbon lattice. Direct experimental evidence of thermal vacancies in graphite has so far not been obtained, but it is possible that in the near future they will be revealed from observations of moiré patterns in electron micrographs[14]. UBBELOHDE[15] has discussed the possible effects of such ' holes ' in leading to a loss of aromatic resonance and in providing trapping sites for unpaired electron spins. In the same paper Ubbelohde proposed the existence of ' claw ' defects which are ruptures in the network caused by repulsion between saturated carbon atoms following bond rupture at the edge of the network. The buckling of the layers would lead to a loss of resonance and also to a modification of the chemical reactivity of graphite.

Vacancies are produced in appreciable concentration when graphite is irradiated with neutrons or other high-energy particles due to displacement of carbon atoms from their normal sites. The displaced atoms initially reside in interstitial sites between the layer planes, causing an increase in the layer spacing, but tend subsequently to return to network sites. Discussion of the effects of radiation damage on structural and physical properties will be given in *Part III* of this series.

Dislocations

Polygonal and circular growth spirals on certain natural and synthetic crystals of graphite were reported by HORN[16] in 1952. Since then there have been several studies of dislocations using electron microscope techniques[14,17-20]. Many structural irregularities have been observed including laminar cleavage of spiraled crystals along the basal plane and networks of hollow dislocations. Recently KENNEDY[21] has suggested that the principle twinning characteristic of graphite can be attributed to an array of partial dislocations and that the movement of a tilt boundary can alter the relative proportion of the rhombohedral and hexagonal forms in the graphite lattice.

In view of the fact that the step-height of growth spirals may reach 300 Å[17] it is possible that these dislocations may influence the mechanism of electrical transport in the *c*-axis direction. This point has not yet received serious consideration but may well prove to be important if the density of spiral growths is sufficiently high[22].

Substitution Impurities

Substitution compounds in which foreign atoms, such as boron, aluminium, nitrogen, phosphorus *etc.* replace carbon atoms in the graphite lattice would be analogous to the *p*- and *n*-type impurity compounds well known in conventional semiconductors. BOWMAN and KRUMHANSL[23] have repeatedly heated graphite with flocculant metallic boron to 3000°C and conclude from changes in the Hall coefficient that the boron substitutes in the network. Other workers[24-26] have reported that the presence of boron lowers the electrical resistance of graphite and carbon, and SHEPARD, PATTIN and WESTBROOK[27] have described a thermocouple constructed from graphite and boron-doped graphite. Due to the apparent ease with which at least boron can enter the lattice (although no structural proof has been advanced to date) it is highly likely that substitutional impurities are present in both natural and synthetic graphite. Such impurities could have

a significant effect on the concentration of current carriers without drastically perturbing the crystal lattice, as is the case of the interstitial crystal compounds to be described later.

In summary it may be suggested that perfect single crystal graphite is probably extremely rare, if not unknown. Crystals which pass the test of x-ray diffraction may still contain defects which could modify physical and chemical properties. A schematic representation of some of the different types of defect is given in *Figure 2*.

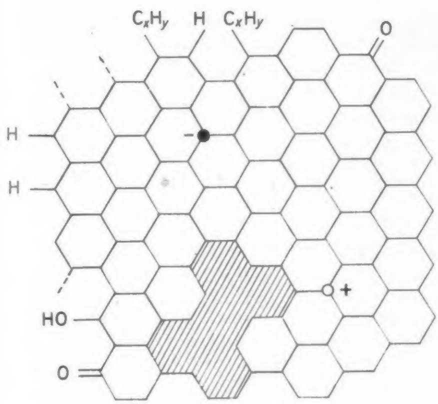

Figure 2. Schematic representation of some possible chemical and structural defects in graphite. (O^- *=pentavalent electron donor atom e.g.* P, *and* O^+ = *trivalent electron acceptor atom e.g.* B; *the shaded part represents a 'hole' caused by two adjacent carbon vacancies*)

The Preparation of Graphite

The major problem in the synthesis of near-ideal graphite is that once graphitization has taken place it is very difficult subsequently to produce marked changes in its bulk structure. The stages involved in the conversion of a polycrystalline matrix into a single crystal may be schematically represented as follows:

Since graphite liquifies only at around 4000°K under a pressure of about 100 atmospheres[28] conventional methods of single crystal growth cannot be applied. Heat treatment to 3000°C and above improves the crystal perfection and increases the crystallite size but it rarely has much effect on the mutual orientation of the crystallites. Sintering in the ceramic sense does not occur and there is no striking reduction in the porosity of a material (this may in part be influenced by the marked anisotropy of thermal expansion of graphite[29]).

The result of these limitations is that each different method of preparing graphite produces a characteristic type of product which only in certain cases may approximate closely to the perfect crystal. Many materials show striking departures from ideality both in respect of crystal defects and the presence of a significant proportion on non-graphitic carbon.

Industrial Bulk Graphite

Graphite which is manufactured in great quantity for the electrical, refractory and atomic reactor industries is prepared basically from a composite mixture of carbon powder, of carefully controlled particle size, and a binder. The carbon powder may be obtained from a wide variety of sources, for example, lampblack, gas black, retort carbon, anthracite, cokes from pitch and heavy refinery oil and natural graphite flakes. The binder usually consists of pitch or tar. The mixture of carbon powder, binder and sometimes up to 10 per cent of lubricating oil is extruded or pressed to the required shape. The compact is then slowly heated to around 750°C; above about 400°C the binder hardens and gases are evolved. Often the product from the first firing is impregnated with further pitch and refired. Finally, the product is heated in a graphitizing furnace to between 2000° and 3000°C when the major proportion of the carbon is converted to graphite. A high purity material containing 20 parts per million or less of ' ash ' may be obtained by carrying out the final firing in a purifying atmosphere containing chlorine and fluorine[30]. A firing cycle may take anything up to six weeks to complete.

Graphite prepared in this way consists of a polycrystalline assembly of crystallites, sometimes having a high degree of crystal perfection, plus usually a small percentage of cross-linking intercrystalline carbon. As a result of the method of forming the compact the final product may exhibit a certain degree of preferred orientation of the crystallites. Extrusion tends to orient the crystallites parallel to the extrusion direction whereas pressing tends to orient them perpendicular to the pressure direction. The degree of preferred orientation may be assessed from the ratios of the intensity

of the (002) basal plane reflections, of the specific electrical resistances or of the thermal expansions parallel and perpendicular to the directions of extrusion of pressure[31]. The bulk density of industrial graphite is usually in the range 1·6 to 1·9 g/cm^3 which means that there is a bulk porosity of around 30 to 25 per cent. This, together with intercrystalline effects, has a deleterious influence on such properties as electrical resistance and thermal conductivity.

Pyrolytic Graphite

A dense form of highly anisotropic graphite is obtained by the thermal cracking of a gaseous hydrocarbon at low pressure onto a graphite surface heated electrically to around 2150°C (BROWN and WATT[32], where further references are given). The deposit of graphite consists essentially of an assembly of crystallites highly aligned with respect to the surface of deposition. Properties measured in the direction parallel to this plane in many cases approach closely those of ideal graphite in the *a*-axis direction[32-34]. The bulk porosity of the material is about 1·5 per cent or less. A remarkable feature of pyrolytic graphite, according to commercial literature from the Raytheon Company, U.S.A., is that the strength-to-weight ratio far exceeds any known material at temperatures around 2000°C.

Pyrolytic graphite prepared from methane at 2150°C, and also a more perfect form obtained by the high temperature recrystallization of this material[34], has proved to be of considerable use in studies of the anisotropic electronic properties of graphite[35] and of its interstitial crystal compounds[36].

Kish Graphite

Crystalline but rather impure graphite called Kish is obtained in the manufacture of cast iron when excess carbon crystallizes from the saturated iron. On purification by acid washing in HCl and HF or by heating to 2800°C a product is obtained which has an interlayer spacing of 3·354 Å and is similar in appearance to natural graphite flakes[37].

Synthetic Single Crystal Graphite

FOSTER, LONG and STUMPF[38] have reported the production of pure single crystal graphite by the thermal decomposition of single crystal aluminium carbide. This was made by heating atomized aluminium powder and lampblack at 1800°C in argon, followed by heating a compact of the product to 2100°C. On continued heating to 2500°C the aluminium carbide, Al_3C_3, decomposed with the volatilization of the aluminium leaving in favourable cases a single crystal of graphite. Crystals up to 0·25 in. long were prepared having an interlayer spacing of $3{\cdot}3545 \pm 0{\cdot}0005$ Å. Although other properties of these crystals have not been published it may be anticipated that they will prove to be useful for investigations of the properties of graphite and of its compounds.

Structural and Physical Changes during Graphitization of Carbon

During the past twenty years there have been many investigations into the changes of structure and of physical properties when a carbonaceous material is heated in an inert atmosphere in the range 400° to 3000°C. For most carbons progressive heating from about 500°C causes a fairly smooth change from small ring structures through larger, but grossly defective, carbon hexagon networks until finally, with the almost complete elimination of hydrogen and other forms of chemical and lattice defects, crystallites of near-ideal graphite are formed. This work has been of great value in advancing our knowledge of the influence of various types of defects on the properties of graphite.

Structural Changes

X-ray diffraction studies[11,39,40] have shown that carbon which has been heated to the point of incipient graphitization (*i.e.* in the region of 1600°C) consists of small randomly oriented packets of graphite-like layers having an interlayer spacing of 3·44 Å. This turbostratic structure gives discrete (002) and (004) basal plane reflections but only diffuse unsymmetrical (*hk*) bands in the approximate position of the (100) and (110) reflections of graphite. With progressive heating the three dimensional order within the packets increases, as shown initially by a modulation of the (*hk*) bands into discrete (*hkl*) reflections and later by the appearance of high order (00*l*) and (*hkl*) reflections. From an analysis of the intensity distribution of the (00*l*) reflections, after making corrections for various instrument and sample effects, it is possible[11,40,41] to determine the *c*-axis crystallite height (*Lc*) and the mean interlayer spacing. Similarly from the (*hk*0) lines the mean crystallite diameter (*La*) can be determined. Exact determinations of these parameters require the use of a Fourier analysis of the intensities to separate strain broadening from particle size and stacking faults. As already stated the *La* and *Lc* dimensions increase, and the mean interlayer spacing decreases, progressively during graphitization.

Many factors influence the rate and extent of graphitization of a carbon and in fact some carbons do not become graphitic even at the highest temperatures. For example, the char obtained from polyvinyl chloride $(C_2H_3Cl)_n$ graphitizes easily whereas that from polyvinilidine chloride $(C_2H_2Cl_2)_n$

does not[42]. The difference in behaviour is probably due to the fact that in polyvinyl chloride on pyrolysis the chlorine may be evolved as HCl while sufficient hydrogen may be retained in the char to aid subsequent graphitization. This is not possible in polyvinilidine chloride, however, as there is only sufficient hydrogen to combine with the chlorine. Other factors which influence graphitization are impurities, such as silica, which are known to catalyse crystallization[43], and the degree of preferred orientation of the individual packets of parallel carbon layers.

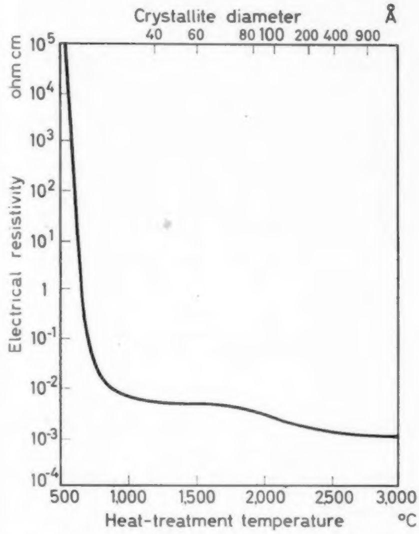

Figure 3. Room temperature electrical resistivity of a graphitizable carbon as a function of the heat-treatment temperature (MROZOWSKI[44], *courtesy Phys. Rev.*)

Physical Changes

Striking changes in electronic, thermal and magnetic properties occur during graphitization. *Figure 3* illustrates the room temperature electrical resistivity of a graphitizable carbon as a function of the temperature of heat-treatment (*Ht*)[44]. The value of $\sim 8 \times 10^{-4}$ ohm cm at $Ht = 3000$°C is typical for a polycrystalline graphite. Similar changes in the thermoelectric power[45] and Hall coefficient[46] are illustrated in *Figure 4*. In *Figures 3* and *4* an estimate of the *La* dimension of the crystallites[47] is indicated on the upper abscissa.

An interpretation of the mechanism of electrical transport in carbons heated in the range 600° to 3000°C has been given by MROZOWSKI and coworkers[44–48] in terms of an energy band scheme in which the energy gap between lower and upper bands progressively decreases until in the limit the band structure of ideal graphite is reached. Although it is difficult to reconcile the use of band models for grossly imperfect carbons of small crystallite size, qualitatively the interpretation serves as a very useful basis for the discussion of experimental results.

The change in the thermoelectric power and Hall coefficient from negative in the low *Ht* range to positive at higher temperatures is attributed on the Mrozowski model to an increase in the number of positive carriers of electricity (holes) in the lower band as a result of the creation of electron trapping centres when peripheral hetero-atoms, *e.g.* hydrogen, oxygen or nitrogen, are thermally expelled from the structure. With increasing *Ht* two mutually opposing effects take place; (*1*) the hexagon networks grow in size, so that the relative proportion of peripheral electron traps decreases, and (*2*) the energy gap between lower and upper bands decreases, which allows an increasing number of electrons to be thermally excited to the upper band. Since room temperature electrons have a greater mobility than holes, with increasing *Ht* the dominant current carriers change from holes to electrons; this results in a peak in the plots of thermoelectric power and Hall coefficient (*Figure 4*) followed by a decrease through zero to negative values. The negative

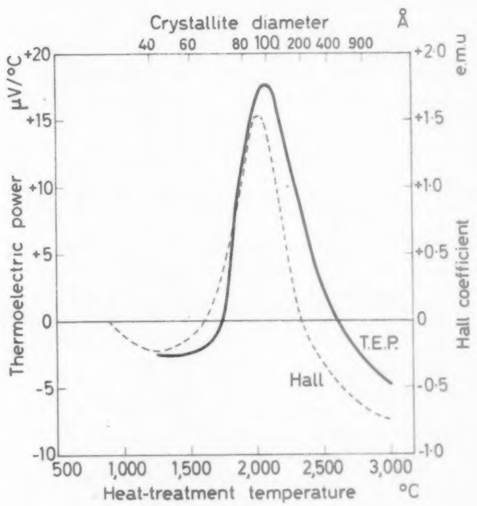

Figure 4. Schematic plot of the room temperature thermo-electric power[45] and Hall coefficient[46] of graphitizable carbon as a function of the heat-treatment temperature

values of the 3000°C heat-treated material approach the values for ideal graphite in the *a*-axis direction.

The change in the room temperature magnetic susceptibility of carbons as *Ht* is raised above 1400°C (*Figure 5*) is another example of the electronic changes that accompany graphitization[49]. The limiting value of about $-7{\cdot}5 \times 10^{-6}$ e.m.u./g represents the value for an assembly of randomly oriented graphite crystallites, but the detailed shape of the magnetic susceptibility curve still requires refinements in the theory of the diamagnetism of carbon for its complete explanation[49,50].

Mechanical Properties of Graphite

Due to limitations mentioned previously very little research on the mechanical properties of graphite has been carried out on single crystals. Polycrystalline graphite contains a high percentage of pore space which can act in different ways; on the one hand the pores can interrupt the relaxation of stress (at crystallite boundaries) whilst on the other they can provide regions for stress relief, especially at high temperatures where thermal expansion effects are pronounced. It is not always possible, therefore, to relate observed mechanical properties to the ideal graphite structure.

Hardness and Friction

Whereas imperfectly graphitized carbons are poor lubricants, difficult to machine and very hard, high temperature polycrystalline graphite is an excellent lubricant that is easily machined and has a low hardness of around one on the Mohs scale. This bulk low value is associated with the good cleavage of crystallites parallel to the basal place. In the perpendicular direction the crystallites are extremely strong, having a hardness quoted as high as nine on the Mohs scale[25]. This is presumably related to the difficulty of rupture of primary valency bonds within the carbon layers.

In recent years the popular view that the lubricating properties of graphite arises from the low friction coefficient between carbon layers *within* a crystallite has been challenged by experiment. Thus SAVAGE[51] has shown that at room temperature the presence of water vapour or ammonia, acetone, benzene *etc.* were essential for good lubrication, and that frictional wear was rapid between graphite surfaces in vacuum or in dry hydrogen or nitrogen. He suggested that the normal lubrication afforded by graphite was due to the formation of a thin layer of water vapour *etc.* held at highly reactive free valency bonds created when misaligned crystallites are broken during friction. On the other hand BOLLMANN and SPREADBOROUGH[52] have proposed a roller mechanism, based on the evidence of electron micrographs, whereby lubrication is achieved by the rolling up of packets of layers which then act as roller bearings. It is claimed that such a mechanism is able to reconcile the experimental data at

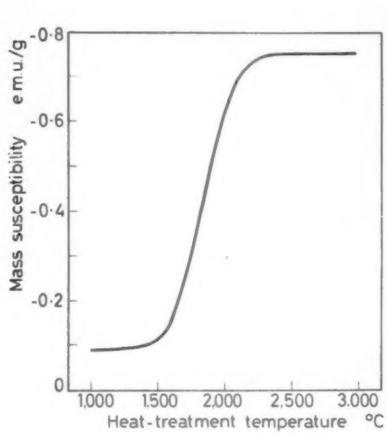

Figure 5. The mass susceptibility of graphitizable carbons as a function of the heat-treatment temperature (PINNICK[49], *courtesy Phys. Rev.*)

present available[53]. Clearly further work with single crystals is necessary to establish the precise origin of the low frictional coefficient of graphite crystallites

Compressibility

The direct mechanical determination of the anisotropy of compressibility of graphite is not possible due to plastic flow. However, RILEY[54] has estimated the linear compressibilities in the *a*- and *c*-axis directions from x-ray measurements of the thermal expansions by using a modification of the Grüneisen and Groens theory, which correlates the thermal expansion of hexagonal crystals with their elastic modulii and heat capacities. Using BASSET's[55] direct experimental value of $44{\cdot}9 \times 10^{-13}$ cm²/dyne for the room temperature compressibility of bulk graphite ($2Ka + Kc$) Riley calculated the linear compressibilities to be $Ka = -2{\cdot}5$ and $Kc = +50$ ($\times 10^{-13}$ cm²/dyne). These values clearly accord with the anisotropy of bond strength in the graphite crystal; for bulk graphite the compressibility is mainly associated with the interlayer compression.

Young's Modulus and Tensile Strength

Polycrystalline graphite is not perfectly elastic, even at room temperature, as irreversible changes occur due to plastic flow. Determinations of the Young's

modulus of different graphites obtained from measurements of the velocity of sound in the material, from flexural and longitudinal vibrations and from stress–strain curves at low applied stresses all show good agreement[56,57]. Values for different graphites measured by DAVIDSON, LOSTY and ROSS[57] lie in the range 7 to 22 $\times$ 10^{10} dynes/cm^2; the high value refers to a specimen made from natural graphite which presumably contained a high proportion of layer planes parallel to the direction of measurement. RILEY[54] calculated that the elastic modulus in the direction of the layers was very much higher than in the perpendicular direction.

The tensile breaking stress of polycrystalline graphite exhibits a remarkable increase with temperature up to about 2500°C, when the breaking stress can be as much as double that at room temperature[58]. In the temperature region above about 1600°C polycrystalline graphite is one of the strongest materials known. Presumably pyrolytic graphite is even stronger and it may well have important applications as a high temperature structural material.

References

1 WALKER, P. L., RUSINKO, F. and AUSTIN, L.G. *Advances in Catalysis II* New York: Academic Press, 1959, 133
2 SMITH, R. N. *Quart. Rev. chem. Soc.* (1959) **13,** 287
3 BERNAL, J. D. *Proc. Roy. Soc.* (1924) **A 106,** 749
4 LIPSON, H. and STOKES, A. R. *Nature, Lond.* (1942) **149,** 328
5 BOEHM, H. P. and HOFMANN, U. *Z. anorg. Chem.* (1955) **278,** 58
6 LAVES, F. and BASKIN, Y. *Z. Krist.* (1956) **107,** 337
7 BACON, G. E. *Acta Cryst., Camb.* (1952) **5,** 392
8 HAERING, R. R. *Canad. J. Phys.* (1958) **36,** 352
9 LUKESH, J. S. *J. chem. Phys.* (1951) **191,** 383
10 BISCOE, J. and WARREN, B. E. *J. appl. Phys.* (1942) **13,** 364
11 FRANKLIN, R. E. *Acta Cryst., Camb.* (1951) **4,** 253
12 BACON, G. E. *Acta Cryst., Camb.* (1951) **4,** 558
13 HOVE, J. E. *Industrial Carbon and Graphite.* London: Soc. Chem. Ind. (1958), 501
14 DAWSON, I. M. and FOLLETT, E. A. C. *Proc. Roy. Soc.* (1959) **A 253,** 390
15 UBBELOHDE, A. R. *Nature, Lond.* (1957) **180,** 380
16 HORN, F. H. *Nature, Lond.* (1952) **170,** 581
17 TSUTUKU, T. *J. phys. Soc. Jap.* (1957) **12,** 778
18 TSUTUKU, T. *Proc. 3rd Carbon Conference, Buffalo, New York,* 1959, 433
19 HASHIMOTO, H. and UYEDA, R. *Acta Cryst., Camb.* (1957) **10,** 143
20 HENNIG, G. R., DIENES, G. J. and KOSIBA, W. (1958) *International Conference on Peaceful Uses of Atomic Energy.* New York: United Nations, Report A/CONF. 15/P/1778
21 KENNEDY, A. J. *Proc. Phys. Soc.* (1960) **75,** 607
22 AXELROD, N. N. and DEXTER, D. L. *Bull. Amer. phys. Soc.* (1956) **1,** 119
23 BOWMAN, J. C. and KRUMHANSL, J. A. *J. phys. chem. Solids* (1958) **6,** 367
24 WEINTRAUB, E. *Trans. Electrochem. Soc.* (1909) **16,** 182
25 GRISDALE, R. O., PFEISTER, A. C. and VAN ROOSBROEK, W. *Bell System Tech. J.* (1951) **30,** 271
26 ALBERT, P. and PARISOT, J. *Proc. 3rd Carbon Conference,* Buffalo, New York, 1959, 467
27 SHEPARD, R. L., PATTIN, H. S. and WESTBROOK, R. D. *Bull. Amer. phys. Soc.* (1956) **1,** 119
28 BASSET, J. *Brennst Chemie* (1942) **23,** 127
29 MROZOWSKI, S. *Proc. 1st Carbon Conference,* Buffalo, New York, 1956, 31
30 ODENING, C. A. and BOWMAN, J. C. *Industrial Carbon and Graphite.* London: Soc. Chem. Ind., 1958, 537
31 ALI, D., FITZER, E. and RAGOS, A. *Industrial Carbon and Graphite.* London: Soc. Chem. Ind., 1958, 135
32 BROWN, A. R. G. and WATT, W. *Industrial Carbon and Graphite.* London: Soc. Chem. Ind., 1958, 86
33 BROWN, A. R. G., WATT, W., POWELL, R. W. and TYE, R. R. *Brit. J. appl. Phys.* (1956) **7,** 73
34 BLACKMAN, L. C. F. and UBBELOHDE, A. R. in preparation
35 BLACKMAN, L. C. F., DUNDAS, P. H. and UBBELOHDE, A.R. *Proc. Roy. Soc.* (1960) **A 255,** 293
36 BLACKMAN, L. C. F., MATHEWS, J. F. and UBBELOHDE, A. R. *Proc. Roy. Soc.* (1960) **A 255,** 15 and in press
37 WALKER, P. L. and IMPERIAL, G. *Nature, Lond.* (1957) **180,** 1185
38 FOSTER, L. M., LONG, G. and STUMPF, H. C. *Amer. Mineralogist* (1958) **43,** 285
39 STEWARD, E. G. and DAVIDSON, H. W. *Industrial Carbon and Graphite.* London: Soc. Chem. Ind. 1958, 206
40 HOUSKA, C. E. and WARREN, B. E. *J. appl. Phys.* (1954) **25,** 1503
41 BOWMAN, J. C. *Proc. 2nd Carbon Conference,* Buffalo, New York, 1956, 59
42 FRANKLIN, R. E. *Proc. Roy. Soc.* (1951) **A 209,** 196
43 STEWARD, E. G. and COOK, B. P. Unpublished work
44 MROZOWSKI, S. *Phys. Rev.* (1952) **85,** 609 and *errata ibid.* (1952) **86,** 1056
45 LOEBNER, E. E. *Phys. Rev.* (1956) **102,** 46
46 KMETKO, E. A. *J. chem. Phys.* (1953) **21,** 2152
47 MROZOWSKI, S. and CHABERSKI, A. *Phys. Rev.* (1956) **104,** 74
48 MROZOWSKI, S. *J. chem. Phys.* (1953) **21,** 492
49 PINNICK, H. T. *Phys. Rev.* (1954) **94,** 319
50 PINNICK, H. T. and KIVE, P. *Phys. Rev.* (1956) **102,** 58
51 SAVAGE, R. H. *J. appl. Phys.* (1948) **19,** 1
52 BOLLMANN, W. and SPREADBOROUGH, J. *Nature, Lond.* (1960) **186,** 29
53 BOWDEN, F. P., YOUNG, J. E. and ROWE, G. *Proc. Roy. Soc.* (1952) **A 212,** 439
54 RILEY, D. P. *Proc. phys. Soc.* (1945) **57,** 486
55 BASSETT, J. *C. R. Acad. Sci., Paris* (1941) **213,** 829
56 WOODS, W. K., BUPP, L. P. and FLETCHER, J. F. *Int. Conference on Peaceful Uses of Atomic Energy.* New York: United Nations (1956) **7,** 665
57 DAVIDSON, H. W., LOSTY, H. H. W. and ROSS, A. M. *Industrial Carbon and Graphite.* London: Soc. Chem. Ind. 1958, 551
58 MALSTRÖM, C., KEEN, R. and GREEN, L. *J. appl. Phys.* (1951) **22,** 593

VIRUS INTERFERENCE AND INTERFERON

A New Approach to Virus Chemotherapy

D. C. BURKE

*National Institute for Medical Research**

It is well known that virus infections are resistant to drugs and antibiotics. Reasons for this are discussed, and the discovery of interferon, which acts as a viral antibiotic is described. Interferon, a product of the virus interference phenomenon, is a protein which can block the multiplication of a number of animal viruses. Recent work on its preparation, properties and mode of action are described.

THE last thirty years have seen spectacular progress in the successful chemotherapy of many diseases. The great variety of synthetic drugs which have been developed, together with the wide range of antibiotics available, have led to effective control of many bacterial and protozoal infections. However, the combating of virus diseases has been much less successful. This is not because virus infections are unimportant—the cost to the community of the Asian influenza epidemic is well known, and the loss due to virus infections of agricultural products is many million pounds per year. Neither does this failure stem from lack of effort, for many hundreds of drugs and antibiotics have been screened for possible anti-viral action. The difficulty lies in the way viruses multiply. Bacteria have a metabolism of their own, differing in some points from that of the host, and it is often possible to find a drug or antibiotic which will affect the bacterial metabolism selectively, leaving the host unharmed. Virus multiplication, however, is so closely bound up with the metabolism of the host that it is very difficult to find an agent which affects one and not the other.

There is much yet to be learned about the course of virus multiplication, but the broad outlines are clear. Shortly after infection there follows a so-called 'eclipse-phase', when little or no virus can be recovered from the cell, probably because the virus splits up after entry and before multiplication starts. At the end of the eclipse phase virus particles appear within the cell, and are then released into the surrounding fluid. Multiplication of the virus often causes damage to the host, and is the cause, directly or indirectly, of the symptoms of the disease. With infections due to some viruses, such as the virus causing cold sores, herpes simplex, the metabolism of the virus and cell is so closely intertwined that the virus stays within the cell, dividing as fast as the cell, and causing no visible disturbance for long periods, until some external stimulus provokes a burst of virus multiplication. In the case of herpes simplex this causes cell damage and the appearance of the typical cold sore.

Many viruses, particularly the smaller ones, are comparatively simple chemically, being made up largely of nucleic acid and protein. Both of these are long chain-like molecules, and by varying the type and sequence of the links it is possible to obtain a great number of similar but not identical products. The protein and the nucleic acid of a particular virus are different from those of other viruses or from those of the host cells, even though the same links are used in each case. Now viruses have no energy-generating system and few enzymes, certainly not enough to carry out the wide variety of chemical transformations necessary for the production of new virus particles. The energy-generating system, many of the enzymes, and the small molecules used in building up proteins and nucleic acids are all available within the host cell, and the virus, living parasitically, is able to make use of them. The virus has to supply instructions to the cell for the production of new virus particles, and these instructions are carried by its nucleic acid. The virus nucleic acid is able to stimulate the production not only of more virus nucleic acid, but also of virus protein and any other necessary components. Recently it has been shown that the nucleic acid, when carefully removed from the virus, is itself infective, illustrating its key role in virus reproduction. Much recent work, therefore, has gone into the synthesis of compounds which will interfere with the functioning of nucleic acid, two of the more successful examples being 5-bromouracil and 8-azaguanine, which are effective against some bacterial and plant viruses respectively. As yet no drug or antibiotic has been found effective against those viruses which infect animals or men.

Attention has therefore turned to prevention rather than cure, and much effort has been expended in the last few years in developing vaccines against virus diseases, thus making use of the host's ability to produce antibodies to viruses. The success of the

*Dr BURKE is now at The Department of Biological Chemistry, The University, Aberdeen. This article was submitted in 1959.

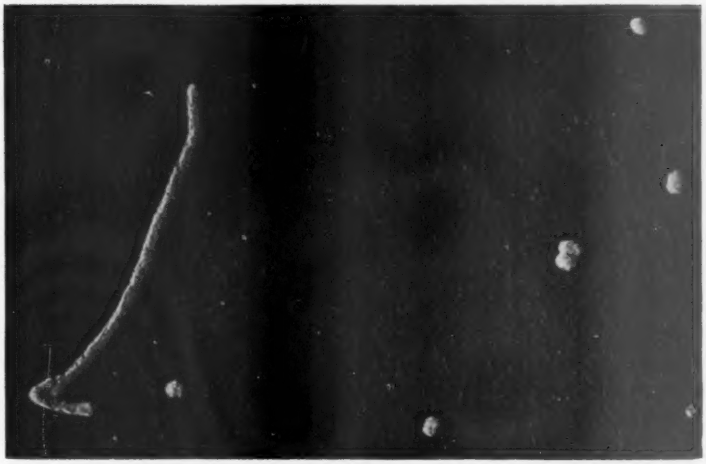

Figure 1. Metal-shadowed electron microphotograph of Influenza A virus showing both spherical and filamentous forms (× 35,000) (*Courtesy* R. C. VALENTINE)

anti-poliomyelitis vaccine is well known, but this vaccine also illustrates one of the disadvantages of this type of approach. Vaccines are so specific in their action that all three types of poliomyelitis virus have to be used in vaccine production in order to give complete protection. The protection does not take effect until after about a fortnight, often after protection is most needed, and does not last indefinitely.

There is another way of preventing virus multiplication, and that is by making use of another virus, working rather on the principle of 'set a thief to catch a thief'. If one virus is multiplying within a cell it will often block the growth of a second virus, called the challenge virus, whether the second virus is related immunologically to the first or not. This protective action is known as virus interference.

Virus Interference

FINDLAY and MACCALLUM in 1937 were the first to demonstrate virus interference unequivocally[1]. They showed that infection of monkeys with Rift Valley fever virus protected them from subsequent infection with yellow fever. Since the two viruses are immunologically unrelated, the protection could not be due to the effect of antibodies. The experimental system was later simplified in two ways; first by the use of the developing chick embryo as the source of living cells, and second by the discovery that carefully inactivated influenza virus, was as good an interfering agent as live influenza virus[2]. Chick embryos are, of course, much simpler and cheaper to use than monkeys. and also have the advantage of not producing antibodies. The use of inactivated virus has several advantages: only one virus is multiplying, thus simplifying the ultimate virus assay; the inactivated virus is more inert biochemically, making it easier to find the place where the blockage of virus growth occurs; and the interfering virus does not cause gross damage to the cell which would itself hinder the growth of the challenge virus. The amount of interference has usually been measured by reduction in the yield of challenge virus.

Interference by inactivated influenza virus in the chick embryo has been studied extensively, and a number of facts have been established. It has been shown that the interfering ability is a property of the virus particle, that protection is afforded against a wide variety of challenge viruses, and that the protective action takes some hours to develop[3]. Most of the work has been done with inactivated influenza virus, but several other inactivated viruses have been shown to induce interference as well[4].

The interfering virus could block virus multiplication during any of the three phases of the cycle; as the virus enters the cell, while it is within the cell, or as the new virus leaves the cell. Large doses of inactivated virus can prevent the challenge virus entering the cell by destruction of receptors on the cell surface[5], but this effect is a rapid one and does not explain the several hours' incubation needed for the system most commonly studied. Since there is no evidence of accumulation of virus within the cell as a result of interference, the block must occur before the virus particles are completed. The need for several hours' incubation at 37°C suggests that

some metabolic process must be completed before interference is induced. The cellular pathway that is blocked must be common to a number of viruses, for inactivated influenza virus will interfere not only with influenza A and B but also with such unrelated viruses as western equine encephalitis[6] and vaccinia[7]. Influenza virus contains ribonucleic acid, while vaccinia contains deoxyribonucleic acid, and it is probable that this fundamental difference in the type of nucleic acid is reflected in the path of intracellular multiplication. We do not know what cellular pathways these two different viruses have in common; the study of virus interference may throw light on the common features. This type of interference—an intracellular phenomenon induced by inactivated virus and directed against a variety of viruses—has been called heterologous interference, and there is evidence that it is mediated through a substance known as interferon.

Interferon

Interferon was discovered by ISAACS and LINDENMANN during a study of interference induced by heat-inactivated influenza virus[8]. They found that when the inactivated virus was incubated at 37°C with the chorio-allantoic membrane of a 10- or 11-day old chick embryo in buffered salt solution, a substance was formed within the cells, and subsequently released into the fluid, which had the property of inducing interference in fresh chorio-allantoic membranes. This substance, different from the inactivated virus used in its preparation, was named interferon, since it seems to be involved in all cases of heterologous interference studied so far. Interferon behaves like a viral antibiotic and therefore its production, properties, and mode of action are being studied intensively.

Two lines of evidence suggest that interferon is the mediator of virus interference. First, it has been produced whenever heterologous interference has been established, and second, it resembles inactivated virus in its action. Influenza virus which has been heated for one hour at 56°C at an alkaline pH is a good interfering agent and leads to the production of interferon. However, after the virus has been heated at 60° it will no longer induce interference or produce interferon. Ultra-violet inactivated virus is known to be a more efficient interfering agent than heat-inactivated virus, and it has also been found to produce more interferon. When influenza virus is irradiated for progressively longer times with ultra-violet light the ability to interfere is gradually lost, and it has been found that the ability of the virus to produce interferon is lost at about the same point[9]. When ultra-violet inactivated virus was diluted in a series of two-fold dilutions and tested for its ability to induce interference and produce interferon, it was found that the virus was able to produce interferon to within one two-fold dilution of its ability to induce interference[10]. Interference can be established by using influenza virus inactivated at 37°C, and by using virus of lowered infectivity

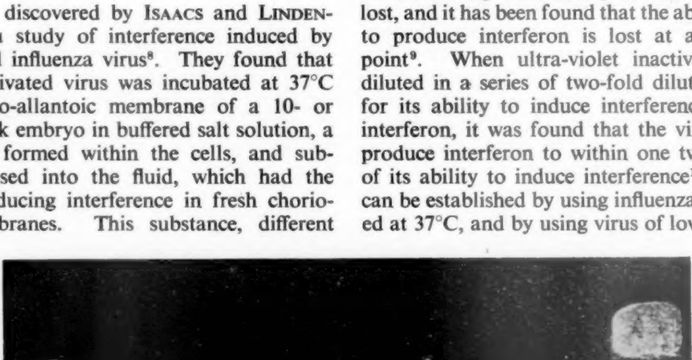

Figure 2. Metal-shadowed electron microphotograph of vaccinia (×*35,000*).
(*Courtesy* R. C. VALENTINE)

(incomplete virus) prepared by the method of VON MAGNUS[11], but not by virus inactivated with 0·02 per cent formaldehyde[12]. In all three cases there is a correspondence between the induction of interference and the production of inferon.

The interference produced by interferon is very similar to that produced by inactivated virus. In both cases several hours' incubation at 37°C is needed, and protection is afforded against the same wide range of viruses. When different strains of influenza virus were compared as to their susceptibility to interferon and inactivated virus, a close correspondence was observed. That is, the strain most susceptible to interference by inactivated virus was also most susceptible to interference by interferon, and *vice-versa*[10]. One other point of similarity was observed; when live virus was added to cells in which interference had been induced either by interferon or by live virus, fresh interferon was produced in both cases[13]. The parallels between the induction of interference by inactivated virus and the production of interferon, together with the similar interfering action of inactivated virus and interferon, strongly suggest that heterologous interference is mediated through interferon.

The production of interferon is not restricted to inactivated influenza virus, for both inactivated Newcastle disease of fowls and inactivated fowl plague virus will produce interferon[12]. Both these viruses are related to influenza, but there is also evidence of the production of an interferon-like substance by a completely unrelated virus, for Ho and ENDERS have found that during the growth of an avirulent chick embryo-adapted poliomyelitis virus in human kidney cells, a substance appeared in the medium which had many of the properties of interferon[14].

While interferon has usually been produced by inactivated influenza virus, it can also be produced by live influenza virus under certain conditions[12,15]. No interferon could be found during the initial phase of virus growth, but after virus growth had begun to fall off, interferon was produced, possibly by the action of the accumulated heat-inactivated virus. It is not known whether these two phenomena are related as cause and effect, but it is possible that interferon may play a part in the spontaneous termination of natural virus infections.

Interferon production is not limited to cells of the chorio-allantoic membrane, for it has also been produced in monkey kidney cells and in calf kidney cells[12]. However although it has not yet been possible to demonstrate any difference between the interferons produced by different viruses, the interferons produced in different cells do differ in some way, as yet unexplained. TYRRELL has found that interferon produced in chick chorio-allantoic membranes was more active when tested in chorio-allantoic membranes than in calf kidney cells and that, conversely, interferon produced in calf kidney cells was more active when tested in these cells than in chorio-allantoic membranes[15]. This effect has also been found using interferons prepared in chick embryo cells and rabbit kidney cells[16].

Mechanism of Interference

We do not yet completely understand either how interferon is produced or how it induces interference. The production of interferon might be explained in at least two ways; interferon could be part of the inactivated virus, removed from the virus within the cell, or it could be produced in the cells as a response to the virus. The latter explanation is much more likely to be true, since it is otherwise difficult to explain why the chorio-allantoic membrane continues to produce interferon for forty-eight hours after an initial treatment with ultra-violet inactivated virus[12].

More light was cast on the production of interferon by some experiments in which its production by ultra-violet irradiated virus was measured[17]. It was found that while unirradiated virus did not produce any interferon within the first twenty-four hours, lightly irradiated virus was an efficient interferon producer. On further irradiation the virus became unable to initiate production of interferon. How could interferon production be initiated by a lightly irradiated virus? It is known that ultra-violet light of the wavelength used (2537 Å) damages the virus nucleic acid[18], and it was suggested that this slightly damaged nucleic acid produced an analogue of some normal virus intermediate, and that this analogue was interferon. However, the nucleic acid of heavily irradiated virus would be too damaged to stimulate interferon production.

If interferon is an analogue of a virus intermediate, it might be possible to produce interferon under conditions where complete virus synthesis is impossible. This can be done, for interferon can be produced in the cells on the chorionic surface of the chorio-allantoic membrane, despite the fact that these cells will only support a partial cycle of virus multiplication[9]. It was also found that when chorio-allantoic membranes, suspended in a buffered salt solution, were treated with heat-inactivated influenza virus so that interference was induced, and interferon was produced, after a second addition of inactivated virus interferon was again produced. The cells, although unable to support the full cycle of virus growth, were nevertheless capable of producing interferon[9].

How does interferon act? The fact that interference is effective against such different viruses as influenza and vaccinia suggests that the block of virus multiplication occurs at a fairly early stage of the cycle, common to both viruses. More information about the mode of action of interferon was obtained from an experiment in which chorio-allantoic membranes were incubated with interferon and then, twenty-four hours later, live virus was added[13]. Little new virus was produced because of the interference induced, but it was found that more interferon was produced. The explanation suggested for this was that the interferon deflected the challenge virus from initiating production of live virus to initiating production of more interferon. In other words, whereas in normal virus growth the live virus provides both the pattern for the new virus and the stimulus to produce it, in the case of interference the pattern is already provided by the interferon, and the challenge virus provides only the stimulus for reproduction of a pattern already present.

Properties of Interferon

There are a number of ways in which interferon differs from the inactivated virus from which it is prepared. It is not adsorbed to chick red cells like the virus, nor is it affected by virus antiserum. Furthermore, interferon can be distinguished from inactivated virus by physico-chemical tests. It is not deposited by centrifugation at 100,000 g for four hours, whereas centrifugation at 23,000 g for thirty minutes is sufficient to remove influenza virus from suspension[19]. This suggests that interferon is either smaller or less dense than the virus particle. Filtration through a series of graded collodion membranes showed that interferon is smaller than the virus, for some interferon passes through a filter of 0·048 μ average pore diameter[17], but influenza virus is held back by a 0·18 μ membrane[20]. This gives an upper limit for molecular weight of interferon of about three million and a lower limit of about 10,000 is provided by interferon being non-dialysable. Interferon is more stable than inactivated influenza virus, for although they are both destroyed by heat, interferon is stable at pH 2 and pH 11, while inactivated virus is rapidly destroyed[9] at both these pH; interferon is quite stable at 2°C or at −70°C[19].

Since the crude interferon solution contains many other substances apart from interferon itself, analysis of the solution cannot tell us anything about the chemical nature of interferon. However, some information about its chemical nature has been obtained by observing the effect of various specific enzymes and chemical reagents on its biological activity. There is good evidence that interferon is protein or partially protein, for it is destroyed by incubation with the proteolytic enzymes, pepsin and trypsin; it is precipitated by saturation with ammonium sulphate, and it is inactivated by shaking with amyl alcohol–chloroform[17]. The enzymes that

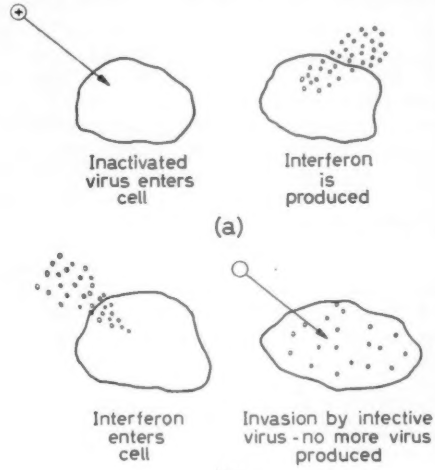

Figure 3. (a) *Interferon production*
(b) *Interferon action*

attack nucleic acids, ribonuclease or deoxyribonuclease, have no effect upon interferon, suggesting that interferon does not contain any nucleic acid. However, it is possible that interferon may contain some nucleic acid protected from enzymatic attack. Interferon is not affected by 0·001 M sodium periodate, a reagent which attacks many carbohydrates, or by the receptor-destroying enzyme from *V. cholerae*, an enzyme which attacks some mucoproteins[9]. A detailed description of the chemistry of interferon must await its isolation in the pure state.

Production of Interferon

Relatively large amounts of interferon are needed both for chemical characterization and for any attempted chemotherapeutic use in animals, and optimal conditions for laboratory-scale preparations have been worked out. Ultra-violet inactivated influenza virus has been found to be by far the most efficient producer of interferon, but the amount of inactivation is critical. Over-irradiation leads to a fall in potency, and must be avoided, but under-irradiation may not render the virus completely non-infective, with the resulting complication of simultaneous virus growth and interferon production. The chick chorio-allantoic membrane provides a good source of cells and has been used almost exclusively up to now. It supplies a large number of

cells (about 10^8 per egg) readily and cheaply with only small egg to egg variation. In this way several litres per week of highly active material can be prepared. However, the chorio-allantoic membrane would probably not be so convenient for large scale work, because of the difficulty of handling large numbers of membranes conveniently in a sterile manner. The interferon thus prepared would be most active in chick cells, and it may be necessary to use animal or human cell lines maintained in tissue culture to produce interferon for chemotherapeutic use in animals and man. The experience gained during anti-poliomyelitis vaccine production would of course be very valuable. There are a number of variables which have not been examined in detail, such as the medium used, and optimum pH and temperature, and the amount of aeration, but it would not be difficult to define these. The size of the interferon molecule rules out any thought of chemical synthesis. The interferon prepared in this way must be concentrated before use for purification work or for use in animals. The methods in use are suitable for laboratory scale but not large scale work, and new methods must be devised.

Possible Uses of Interferon

Virus interference has been demonstrated numerous times in animals but only once in man[21], although it is possible that the prolonged association of adenoviruses with the adenoids and tonsils may give some protection against subsequent infection. There are a number of reasons why interference has not been used therapeutically: the dosage and timing of the challenge and interfering viruses are critical, nearly all the susceptible cells must be protected by the interfering viruses, and even inactivated virus particles are toxic. Interferon does not seem to be toxic, but it shares some of the other disadvantages of interference. Like the virus, interferon must be given some hours before infection and most of the susceptible cells must be involved. Thus it might not be very useful for treating established infections.

Unlike the virus, interferon is susceptible to the attack of proteolytic enzymes; hence it might be destroyed before reaching the site of virus multiplication. This would suggest that local appplication might be better than systemic treatment and it might be tried against such virus infections as herpes simplex or influenza, where the cells involved are exposed, and could be treated directly. The cell specificity of interferon means that it would have to be prepared in different types of cells for use in different hosts. These difficulties should warn us against undue optimism but must not discourage us from further work.

The action of interferon must be thoroughly explored in animals before it can be used in man. It is not yet known how best to administer interferon or what difficulties might arise in the way of toxicity or undesirable side effects. One of the difficulties involved in transferring the study of interferon from a small piece of chorio-allantoic membrane to an animal such as a mouse is the one thousandfold increase in weight. This means that concentrated and purified preparations of interferon will have to be used if results are to be obtained uncomplicated by the effect of impurities. Interferon has been shown to be active in the fertile egg and also locally in the rabbit skin[9]. This is but a beginning, but it is probably along these lines that progress will be made.

Interferon would seem to be important for two reasons; first it represents a new approach to the problem of virus chemotherapy and may lead to the discovery of an effective means of control. Second the study of the formation and action of interferon will increase our understanding of the multiplication cycle of viruses, and therefore improve our chances of being able to stop virus multiplication and prevent its harmful consequences.

References

1 FINDLAY, S. M. and MACCALLUM, F. O. *J. Path. Bact.* (1937) **44**, 405
2 HENLE, W. and HENLE, G. *Amer. J. med. Sci.* (1944) **207**, 705
3 HENLE, W. *J. Immunol.* (1950) **64**, 203
4 LOCKART, R. Z. and GROMAN, N. B. *J. Infect. Dis.* (1958) **103**, 163
5 BALUDA, M. A. *Virology* (1959) **7**, 315
6 HENLE, W. and HENLE, G. *Amer. J. med. Sci.* (1945) **210**, 362
7 DEPOUX, R. and ISAACS, A. *Brit. J. exp. Path.* (1954) **35**, 415
8 ISAACS, A. and LINDENMANN, J. *Proc. Roy. Soc.* (1957) **147**, 258
9 LINDENMANN, J., BURKE, D. C. and ISAACS, A. *Brit. J. exp. Path.* (1957) **38**, 551
10 BURKE, D. C. and ISAACS, A. *Acta Virologica* (1960) in press
11 VON MAGNUS, P. *Acta. path. Microbiol. Scand.* (1951) **28**, 278
12 BURKE, D. C. and ISAACS, A. *Brit. J. exp. Path.* (1958) **39**, 452
13 ISAACS, A. and BURKE, D. C. *Nature, Lond.* (1958) **182**, 1073
14 HO, M. and ENDERS, J. F. *Proc. Nat. Acad. Sci., Wash.* (1959) **45**, 385
15 TYRRELL, D. A. J. *Nature, Lond.* (1959) **184**, 452
16 ISAACS, A. and WESTWOOD, M. A. *Lancet* (1959) 324
17 BURKE, D. C. and ISAACS, A. *Brit. J. exp. Path.* (1958) **39**, 78
18 POWELL, W. F. and SETLOW, R. B. *Virology* (1956) **2**, 337
19 ISAACS, A., LINDENMANN, J. and VALENTINE, R. C. *Proc. Roy. Soc.* (1957) **B 147**, 268
20 ELFORD, W. J., ANDREWES, C. H. and TANG, F. F. *Brit. J. exp. Path.* (1936) **17**, 51
21 SCHLESINGER, R. W., GORDON, I., FRANKEL, J. W., WINTER, J. W., PATTERSON, P. R. and DORRANCE, W. R. *J. Immunol.* (1956) **77**, 352

MAGNETIC PROPERTIES OF EPITAXIALLY GROWN FILMS

O. S. HEAVENS

Department of Physics, Royal Holloway College, University of London

The possible advantages of using epitaxially grown films in studies of thin film properties are discussed with particular reference to magnetic properties. Methods suitable for magnetic measurements are described and a summary of the types of result obtained to date is given. Preliminary results are given of measurements of the Faraday rotation in epitaxially grown nickel films.

ALTHOUGH extensive work has been done on many properties of thin films formed by thermal evaporation, almost the whole of this work has been done with films which are polycrystalline or amorphous. Indeed for many of the reported results, no information at all is available about film structure. The phenomenon of epitaxy, wherein a deposited substance grows with a crystal form controlled by that of the substrate, has been known for upwards of thirty years. The phenomenon enables monocrystalline films of many substances to be produced. Surprisingly, relatively little use has been made of epitaxy as a means of producing films in a crystallographically ordered state. Interest in this aspect of thin film work has grown in the last few years and experiments have now been made on the magnetic, optical and mechanical properties of a few epitaxially grown materials. The purpose of this paper is to discuss the results obtained in studying the epitaxial growth of the ferromagnetic elements, to outline the results to be expected from theory in studies of the magnetic behaviour of films and to discuss the results which have been obtained to date in relation to such theory.

General Comments on Physical Properties and Film Structure

In the past there have frequently been large discrepancies between different observers' results obtained on thin films. These inconsistencies can often be traced to differences in conditions of preparation which have in turn resulted in differences in film structure. These differences may sometimes be considerable. Since the dependence of film structure on deposition conditions is generally neither well known nor well understood, the reasons for discrepancies are frequently obscure. One of the variables which has, in the past, been difficult to control is the residual gas content of films. For feasible rates of deposition of the film, the amount of residual gas which falls on the film during deposition could not be reduced to negligible proportions, if the pessimistic view is taken that all such gas is trapped in the film. Recently, developments in ultra-high vacuum systems have brought the feasibility of performing experiments under much less uncertain conditions than hitherto. As will be shown, results obtained under these conditions are sometimes dramatically different from earlier ones.

One may be tempted to consider that all results obtained under earlier 'dirty' vacuum conditions be ignored and that advantage be taken of the newly-developed techniques to repeat earlier work. In certain fields there is little question but that this counsel of perfection should be followed, particularly in respect of films in the thickness range of a few millimicrons. For thicker films, however, much of the information obtained under earlier, less-than-ideal conditions remains useful and can serve as a guide to future work. In respect of structural properties, the work of LEVINSTEIN[1] indicates wide ranges of deposition parameters over which no significant variations are observed. These experiments were carried out entirely on films deposited on amorphous substrates. The films are either amorphous, in the case of films of high melting-point materials, or polycrystalline with substantially random orientation of crystallites. It is clear that such films may have well-defined properties although the detailed behaviour may be to only a small extent governed by the lattice properties of the material of the film. Thus the near-dielectric optical behaviour of some very thin metal films can be accounted for entirely by the state of aggregation of the film. The optical behaviour bears no recognizable relationship to that of the parent metal. Films of this thickness are substantially non-conducting.

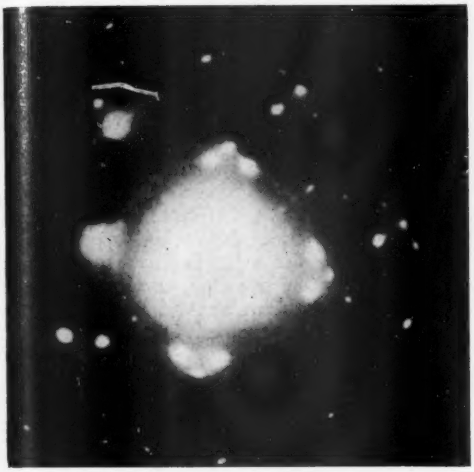

Figure 1. Electron diffraction pattern of Ni film grown on cleaved rocksalt

Whilst the use of epitaxy as a means of producing orientation in films introduces some simplification, the problem of calculating the properties of an aggregated rather than continuous film remains very difficult. Thus the effects of voids, grain boundaries and variation of crystallite size still need to be taken into account. It is found, however, that monocrystalline films of many materials can be made which show very little structural detail under the highest electron microscope magnification. Evidence of dislocation loops and stacking faults is usually present. The films form, however, a reasonably close approximation to the plane parallel-sided, homogeneous slab from which many theoretical treatments begin.

It is likely that the best epitaxially grown single-crystal films contain a rather higher density of faults and dislocations than the best of bulk crystals such as those of silicon and germanium. It also seems probable, however, that the magnetic behaviour of such films will be less violently affected by such crystal faults than, for example, the electrical behaviour (particularly of semiconducting materials), the mechanical properties or the optical scattering properties. Thus whereas the electrical conductivity of an aggregated film is greatly influenced by the scattering of conduction electrons at the film surfaces and grain boundaries, such properties as saturation magnetization and Curie point would not be significantly affected. Moreover, studies of magnetic domains on bulk materials show that magnetic domains frequently cross grain boundaries with no change in direction.

Structure of Epitaxially Grown Films

The structures of films of Fe, Ni and Co, grown on rocksalt crystals, have been investigated by COLLINS and HEAVENS[2] (1957). The general features of the epitaxy of these three metals are (*1*) for substrate temperatures up to ~350°C, polycrystalline films are formed, possibly with a trace of [111] fibre orientation, (*2*) in the region 350–450°C, steadily increasing single-crystal order develops so that, above 450–480°C, completely oriented films form. These remarks apply to films grown on the [100], [110] and [111] rocksalt faces.

Nickel

For film thicknesses in excess of about 20 mμ, parallel orientation of Ni on the three rocksalt faces is obtained. The films show the normal structure of *fcc* nickel and generally show some twinning (*Figure 1*). When films are grown on cleaved and polished rocksalt, the electron diffraction patterns show spots characteristic of the lattice only (*Figure 2*). The appearance of Kikuchi lines indicates a high degree of perfection of the single-crystal film. No evidence has been obtained of hexagonal nickel under these conditions.

Cobalt

Although the stable form of cobalt is hexagonal below 420°C and *fc* cubic above this temperature, films generally consist of mixtures of the two forms, even when deposited at temperatures above 500°C.

Figure 2. Pattern from film grown on polished rocksalt. Note absence of twinning and distortion

The cubic form may be held metastably by the rocksalt influence, changing to polycrystalline hexagonal when the film is removed from the substrate: this behaviour is observed in films less than 20 mμ thick. Thicker films generally show a mixture of orientations together with extensive stacking faults. It has not so far proved possible to obtain stable films in which one single orientation is present.

Iron

Although only one crystal form of iron is observed in epitaxially grown films, a mixture of orientations is obtained, consisting predominantly, in the case of films grown on the cube face of rocksalt, of

Fe (001) [100] || NaCl (001) [100]

and

Fe (001) [100] || NaCl (001) [110]

In addition, small amounts of iron with (111) and [210] planes lying parallel to the NaCl face are observed. The proportions of these orientations do not appear to vary regularly with rate of deposition, substrate temperature or film thickness.

On account of the difficulties experienced in obtaining well-defined single orientations in films of Co and Fe, studies of magnetic behaviour have been confined to nickel and to certain nickel–iron alloys which show epitaxial behaviour similar to that of nickel.

Comments on Expected Thin Film Magnetic Behaviour

Anticipating the stage at which it becomes possible to produce ordered films in thickness down to one monolayer, it is natural to enquire whether such an array of atoms is expected to be ferromagnetic. The problem is a difficult one and has so far been dealt with only for the case of two-dimensional arrays of atoms in the absence of an applied magnetic field. (This is a severe limitation in so far as any determination of magnetic properties must surely entail applying a field.) The linear chain admits of exact solution and has been shown by BETHE[3] not to be ferromagnetic, again for the case of zero applied field. Different treatments of the two-dimensional array yield different answers to the question of whether various types (honeycomb, plain square, hexagonal) of lattice should possess a Curie point. A discussion of the present situation is given by VAN VLECK[4]. A molecular field treatment by VALENTA[5] leads to the result that the Curie temperature for a monomolecular hexagonal layer should be one-half of that of the bulk material. It is clear that measurements on ordered films of thicknesses down to a monolayer are urgently needed in order that some guidance on the validity of the theoretical assumptions be obtained.

In the region of greater thicknesses, say of a few tens of millimicrons upwards, one expects to be able to describe film behaviour on a macroscopic model. Magnetization curves obtained for fine particles and for films of thickness down to 2 mμ (NEUGEBAUER[6]) are found to be practically identical with those of the bulk material. In films of iron, ROSETTE and HOFFMAN[7] find the saturation magnetization *v.* temperature curves to approach those of the bulk for films a few tens of millimicrons thickness. Some anomalous behaviour in these films is thought to be associated with oxidation, which occurred in spite of the use of a protective MgF_2 coating. Thus the crystallites forming thick films may be regarded as possessing the bulk properties. Film behaviour may then be deduced if the (many) factors governing the magnetic behaviour can be assessed. These include the effects of domain structure (if the film is thick enough), anisotropy, strain and magnetostatic effects. In practice these effects may be difficult to calculate. Thus a vacuum-deposited film will be in a state of stress from two causes: (*1*) the differential thermal contraction between film and substrate will introduce a uniform planar tension or compression; (*2*) where the film is deposited in a magnetic field, the resultant unidirectional magnetization will induce a further stress in that direction. In the case of alloys (*e.g.* permalloy) anisotropy may arise from the formation of directed pairs of one of the constituents. This is observed to happen even when deposition takes place in zero field (SMITH[8]). In addition the direction of the condensing vapour stream may induce anistropy (SMITH[8]; PUGH, BOYD and FREEDMAN[9]).

The general features to be expected in thin film behaviour may be elucidated by minimizing the total energy of the film, this energy being made up of (*1*) magnetic field energy; (*2*) domain wall energy; (*3*) crystal anisotropy energy. Under (*3*) is included the anisotropy energy arising from magnetization in directions inclined to easy directions together with stress anistropy arising from magnetostriction and from any applied stresses. Contributions may also be present from stresses due to imperfections and impurities.

Surface anisotropy (NEEL[10]) may also play a significant part although such effects are to date largely obscured by adsorbed gas films.

KITTEL[11] has shown that, for values of anisotropy constants typical of Ni–Fe–Co, the minimum energy configuration for films of thicknesses less than $\sim 10^{-5}$ cm is one in which the magnetization lies parallel to the plane of the film. Since the film thickness is less than the domain wall thickness, the films are expected to be single domains. Thus magnetization

changes occur only by rotation processes against high magnetocrystalline anisotropy forces so that a high coercivity is expected. This behaviour is shown by epitaxially grown nickel (*see* 'Measurements on Epitaxially Grown Films' below).

The precise form of behaviour depends very much on the relative magnitude of the various energy terms above. Thus in cobalt, with a very high anisotropy energy, thick single-domain films may be expected with the direction of magnetization normal to the film. The properties of 80/20 *Permalloy* (about which more is known than about any other material), are dominated by a very low anisotropy energy. Domain walls are observed in films of Permalloy of thickness down to 10–20 mμ: for the thinnest of films, *Neel* walls (in which the magnetization changes direction but with the spins lying parallel to the plane of the film) are observed. In thicker (40 mμ upwards) films *Bloch* walls are observed (METHFESSEL, MIDDELHOEK and THOMAS[12]).

In these and most other measurements, polycrystalline films are used so that magnetic effects observed are averaged over all crystallographic directions. Since the basic quantities influencing magnetic behaviour vary markedly with direction in the lattice, the amount of information to be obtained from measurements on polycrystalline films is limited. The experimental arrangements which have been used in dealing with epitaxial films are described in the following section.

Methods of Preparation and Measurements

Preparation

Since the early report on the magnetic properties of epitaxial nickel films (COLLINS and HEAVENS[13]), in which films were prepared by evaporation from a tungsten filament on to heated rocksalt, a new method of evaporation has been introduced (KELLY[14]; HEAVENS[15]). The metal is evaporated from a molten drop (*Figure 3*) at the lower end of a nickel rod, heating being effected by electron bombardment. The upper molybdenum shield serves for rudimentary focusing and to ensure that the nickel drop cannot be contaminated with any material evaporated from the filament. The lower shield prevents any direct evaporation from the filament from reaching the specimen. At the formation of the drop, some gas is generally released during the melting of new material. If the electron bombardment current is reduced slightly after the drop has formed, the boundary between liquid and solid moves down. It proves easy to maintain this halfway down the drop so that no further gas is released. Although this method has so far been used only in systems at pressures down to 10^{-6} mm Hg, there seems no reason why it should not be satisfactory at even lower pressures. The method obviates any risk of contamination of the film by crucible or filament material.

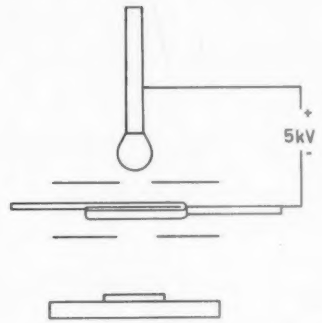

Figure 3. Schematic diagram of electron bombardment evaporation system

Details of the conditions for the epitaxial growth of Ni, Fe and Co have already been given (COLLINS and HEAVENS[2]). It should be noted that relief by annealing of strains and twinning requires a temperature considerably higher (650°C) than that at which epitaxy on rocksalt occurs.

Film Thickness Measurement

Film thickness measurements may be made by Fizeau fringes or the mass of the films determined microchemically. When both measurements are made, the film density is determined. Measurements on iron films (HEAVENS, HINTON and BROWN[16]) show that the density of epitaxially grown films is the same as that of the bulk metal. Furthermore the electron micrographs of epitaxial nickel and iron films show no sign of macroscopic voids, thus supporting the notion that they are of substantially bulk density.

In early experiments on epitaxial nickel films (COLLINS and HEAVENS[13]) the film thickness was deduced from the optical transmission, a calibration between transmission and thickness being made by measurement of films on glass. This was done because the surface of cleaved rocksalt, such as was used in these experiments, is not sufficiently flat for fringe measurements to be made. The validity of this method rests on the assumption that the optical constants of the epitaxially grown films do not differ significantly, over the thickness range considered (20–100 mμ) from those of the polycrystalline material. This assumption is open to some doubt which will be resolved when measurements are made

of the optical constants of nickel films grown on rocksalt. Some differences have been observed in the optical transmission of Ni films grown on cold and on heated mica (HEAVENS[17]).

This uncertainty in thickness measurement is avoided if the film is removed from the rocksalt and picked up on an optical flat. Fizeau fringe measurements may then be made directly. Measurements on iron films (HEAVENS and PANDEYA[18]) established the validity of this procedure.

The mass of Ni and Fe films may be determined (destructively) by microchemical (colorimetric) techniques of commendable sensitivity. The use of nioxime for nickel (JOHNSON[19]) enables some of the difficulties, *e.g.* of colour stability of the complex, to be overcome and allows the mass of 1 cm^2 of film of thickness 10 mμ to be determined to within <1 per cent. A similar sensitivity is available for iron films using tiron. Details of suitable procedures for handling the small quantities of reagents are given by HEAVENS[15].

Magnetic Measurements

These methods fall into two broad groups: (*1*) torsion magnetometer methods, (*2*) alternating field B–H loop methods. The latter method is usually applied to films after removal from the vacuum system and is generally the more convenient if measurements are to be made over a wide temperature range. Torsion magnetometer methods have been used to make measurements on films *in vacuo*. A recent design is described below.

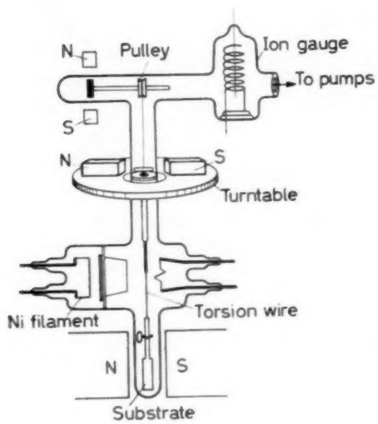

Figure 4. Neugebauer's torsion balance

In the loop tracer described by CRITTENDEN, HUDIMAC and STROUGH[20], a mixed 60 and 180 c/s current provides the magnetizing field. The rate of change of magnetizing current in the neighbourhood of the steep portions of the B–H loop is kept low: the peak voltage applied to the pre-amplifier is thereby reduced and distortion and overloading troubles avoided. The use of an electrometer tube type of circuit results in a noise figure which corresponds to the signal from an iron specimen 0·5 cm wide by 0·35 × 10^{-8} cm thick, if such a specimen were to show the same magnetic behaviour as bulk iron. Further improvements in this circuit are described by ROSETTE and HOFFMAN[7].

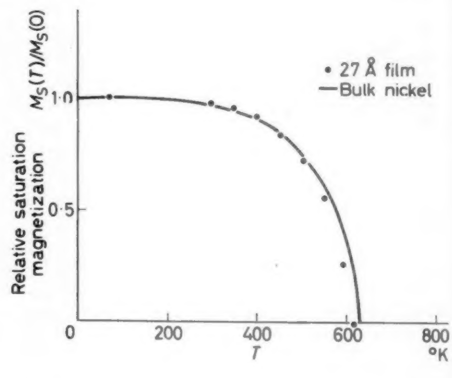

Figure 5. Results obtained for a film 2·7 mμ thick (NEUGEBAUER[6]. *Courtesy John Wiley*)

Two types of torsion magnetometer have been applied to film studies. In the null method of BATE[21], two pairs of coils are used, one to provide the magnetizing field and the second to produce a field gradient at the specimen. The specimen is set to lie parallel to the direction of the magnetizing field before the field is applied. With the field on, the torsion head is rotated to restore the specimen position. The measurement is thus made with the magnetization vector lying in the film.

In the torsion balance used by NEUGEBAUER[6], shown in *Figure 4*, the plane of the specimen is set at 45° to the field direction. When the field is applied, the film tends to turn parallel to the field and is brought back to the 45° position by rotating the torsion head. Under this condition the magnetization vector makes an angle θ with the field direction where

$$\sin\theta = \frac{M_s H \pm [M_s^2 H^2 + 8(2\pi M_s^2 + K)^2]^{\frac{1}{2}}}{4\,(2\pi M_s^2 + K)}$$

M_s is the saturation magnetization of the specimen, K the anisotropy constant and H the applied field. The torque L on the specimen is $MVH \sin \theta$ where V is the volume of the film. For small fields the relation between L/H and H is approximately linear with an $H=0$ intercept given by

$$(L/H)_0 = 0{\cdot}707\ MV$$

At a field

$$H = (2\pi M_s^2 + K)/M_s$$

we have

$$L/H = 0{\cdot}707\ (L/H)_0$$

whence the value of K is determined. For very high fields a saturation torque

$$L_\infty = (2\pi M_s^2 + K)V$$

is obtained. If K is small compared with $2\pi M_s^2$, then

$$M_s(T)/M_s(0) = \{L_\infty(T)/L_\infty(0)\}^{\frac{1}{2}}$$

and the magnetization *v* temperature curve may be determined. *Figure 5* shows the curve obtained for a nickel film 2·7 mμ thick. The full line is the curve for bulk nickel.

Measurements on Epitaxially Grown Films

Coercivity measurements on epitaxial nickel films (COLLINS and HEAVENS[13]) show a considerable rise in H_c as the thickness becomes smaller (*Figure 6*). The films are found to be spontaneously magnetized along a [100] direction: no sign of domain boundaries could be found using the Bitter technique. The dotted curve in *Figure 6* is from measurements on polycrystalline, electrodeposited films, made by DRIGO and PIZZO[22].

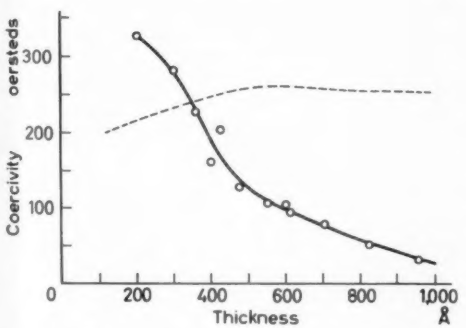

Figure 6. Variation of coercivity with thickness for epitaxially grown Ni *films.* (COLLINS and HEAVENS[13]. *Courtesy Phil. Mag.*)

For single-domain specimens, the coercivity depends on (*1*) the anisotropy energy, (*2*) the shape factor and (*3*) strain energy. If the effects of (*2*) and (*3*) are small, the maximum coercivity to be expected is $\sim 2K/M_s$ (KITTEL[23]). With the value of K for bulk nickel this indicates a maximum coercivity of ~160 oe. The higher value observed suggests that the films may have some strain contribution. Experiments by BOYD[24] on epitaxial films of nickel yield values for the anisotropy constant nearly equal to that for the bulk metal. Substantially similar behaviour is observed by Boyd in various Ni–Fe and Ni–Co alloys. These epitaxial films were annealed at the deposition temperature (~500°C), which is not high enough for the removal of structure faults which are present during deposition. In fact, Boyd's electron diffraction patterns show a certain amount of disordered (polycrystalline) material after anneal.

Magnetic Rotation Experiments

One of the powerful features offered by the use of epitaxial films is that direction-dependent properties may be investigated. Some properties, *e.g.* the Faraday rotation, can be observed only in very thin films. Thus for the first time measurement of this effect in specific lattice directions is made possible. On account of the high optical absorption shown by metals, the thickness range for which Faraday rotation measurements can be made is limited to a maximum of around 40–50 mμ. Plane polarized light is passed normally through the film which is in a magnetic field sufficient to produce saturation normal to the film plane. The measured rotations are of the order of tens of minutes of arc. A photoelectric polarimeter is used.

Typical results for Ni films of thickness 20 mμ grown on the cube, dodecahedral and octahedral faces of rocksalt are shown in *Figure 7*. These measurements were made on films which had not been removed from the NaCl substrate. They are thus in a state of stress determined by the differential thermal contraction of film and substrate. (The intrinsic stress observed by HOFFMAN, ANDERS and CRITTENDEN[25] is observed to be zero in films deposited at substrate temperatures above 250°C: in the experiments reported here, the substrate temperature was 450°C).

At first sight the occurrence of saturation of the Faraday rotation for the (100) films at *lower* fields than for (110) and (111) appears strange since the easy directions for nickel, in increasing order of difficulty, are [111], [110] and [100]. However the reversal of the order of the saturation fields arises from the large magnetostrictive component of the film anisotropy (PUGH[26]). If it is assumed that the strain in the film results from unrelieved differential thermal contraction, then on cooling from 450°C to 20°C the film would develop a strain of ~1·2 per cent. Although high values of strain are observed

in films whose thicknesses are of the order of tens of mμ, values as high as this have not been observed and, from the nature of the interface between the metal film and substrate (wherein on account of mismatch there must be some regions where the binding is weak), it is likely that some relief of strain by slipping will occur. In any case, the very high magnetoelastic energy associated with a strain of ~1 per cent would result in saturation in an applied field of only a few hundred oersteds. From the observed saturation of Faraday rotation (*Figure 7*) at $H = 4300$ oe, for the (100) film, the stress amounts to $1{\cdot}3 \times 10^{10}$ dynes/cm^{-2}, corresponding to a planar strain of 0·29 per cent. For the (110) film, this same stress would result in saturation occurring at an applied field of 4800 oe whilst for a (111) film, saturation should be reached at 5000 oe. The order in which saturation occurs is thus (100), (110) and (111), in agreement with the experimental behaviour shown in *Figure 7*. At the high stresses involved, the crystal anisotropy contribution to the energy is negligible. The above figures are approximate in so far as elastic isotropy is assumed.

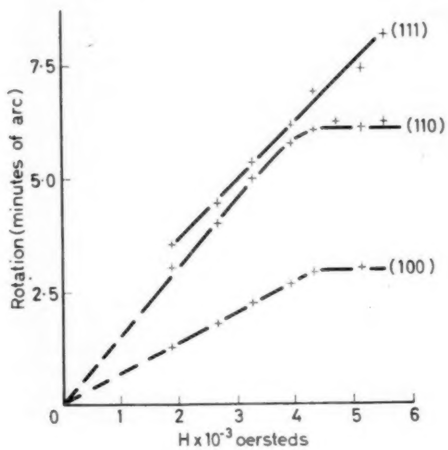

Figure 7. Faraday rotations observed in epitaxial Ni *films.* (HEAVENS and MILLER[27]. *Courtesy John Wiley*)

Conclusions

The use of epitaxially grown films for the study of thin film properties appears to be feasible for certain materials and for the examination of such properties as are not likely to be violently affected by small structure faults. The occurrence of Kikuchi electron diffraction patterns indicates a high degree of crystal perfection: electron microscopy indicates that, under suitable conditions of preparation, continuous film may be formed.

With the state of development of present techniques it is as yet not possible to grow films and remove them from their substrate in ultra-high vacuum systems. The study is indicative, therefore, of properties which may not be violently affected by exposure to air, or of films of such thickness that oxidation or adsorption effects are not important. For such experiments, the availability of films which possess a high degree of crystallographic order is a considerable advantage.

The electron diffraction patterns and Faraday rotation measurements were obtained by R. F. Miller.

References

1. LEVENSTEIN, H. *J. appl. Phys.* (1949) **20**, 306
2. COLLINS, L. E. and HEAVENS, O. S. *Proc. phys. Soc., Lond.* (1957) **B 70**, 265
3. BETHE, H. *Z. Phys.* (1931) **71**, 205
4. VAN VLECK, J. H. *J. phys. Radium* (1959) **20**, 124
5. VALENTA, L. *Izvest. Akad. Nauk. S.S.R., Ser fiz.* (1957) **21**, 879; *Czech. J. Phys.* (1957) **7**, 127, 133
6. NEUGEBAUER, C. A. *Structure and Properties of Thin Films*, New York; John Wiley, 1959, 258
7. ROSETTE, K. H. and HOFFMAN, R. W. *Structure and Properties of Thin Films*, New York; John Wiley, 1960, 370
8. SMITH, D. O. *J. appl. Phys.* (1959) **30**, 264S
9. PUGH, E. W., BOYD, E. L. and FREEDMAN, J. F. *IBM J. Res. Dev.* (1960) **4**, 163
10. NEEL, L. *C. R. acad. Sci., Paris* (1953) **237**, 1468: *J. phys. Radium* (1954) **15**, 225
11. KITTEL, C. *Phys. Rev.* (1946) **70**, 965
12. METHFESSEL, S., MIDDLEHOEK, S. and THOMAS, H. *IBM J. Res. Dev.* (1960) **4**, 96
13. COLLINS, L. E. and HEAVENS, O. S. *Phil. Mag.* (1954) **45**, 283
14. KELLY, J. C. *J. sci. Instrum.* (1959) **36**, 89
15. HEAVENS, O. S. *J. sci. Instrum.* (1959) **36**, 95; *Lab. Pract.* (1959) **8**, 203
16. HEAVENS, O. S., BROWN, M. M. and HINTON, V. *Vacuum* (1959) **9**, 17
17. HEAVENS, O. S. *J. de Phys.* (1959) **20**, 485
18. HEAVENS, O. S. and PANDEYA, D. C. *Nature, Lond.* (1958) **181**, 1394
19. JOHNSON, W. C. *Organic Reagents for Metals*, Vol. I. Essex: Hopkins and Williams, Ltd, 1955
20. CRITTENDEN, E. C., HUDIMAC, A. A. and STROUGH, R. I. *Rev. sci. Instrum.* (1951) **22**, 872
21. BATE, L. (1952) *Ph.D. Thesis*, University of Sheffield
22. DRIGO, A. and PIZZO, M. *Nuovo Cim.* (1949) 6, 387
23. KITTEL, C. *Rev. mod. Phys.* (1949) **21**, 541
24. BOYD, E. L. *IBM J. Res. Dev.* (1960) **4**, 116
25. HOFFMAN, R. W., ANDERS, F. J. and CRITTENDEN, E. C. *J. appl. Phys.* (1953) **24**, 231
26. PUGH, E. W. *Structure and Properties of Thin Films* New York: John Wiley, 1959, 420
27. HEAVENS, O. S. and MILLER, R. F. *Structure and Properties of Thin Films.* New York: John Wiley, 1959 417

MODERN TECHNIQUES IN SOARING FLIGHT

F. G. IRVING

Imperial College of Science and Technology, London

The author gives a scientific account of the art of gliding, describing the sources of atmospheric energy and how they ars best used, the principles involved in the design of gliders to give optimum performance and the instrumentation of gliders.

TO THE uninitiated onlooker, the sight of a glider lazily circling under a swelling cumulus cloud in high summer conjures up a vision of the blissfully contented pilot gazing languidly from his silent cockpit at the sunlit scenery: an elegant mixture of effortless ease, visual beauty and correspondingly sublime thoughts.

Whilst there is a grain of truth in this vision, the somewhat ecstatic state of mind which it implies is usually more pronounced in the pilot's subsequent recollections than during the actual flight. The attainment of a worthwhile performance in a modern glider is quite a complicated technical job. Given a good machine, itself quite a sophisticated device, the process of using it to the best advantage depends to no small extent on good instrumentation supplemented by suitable computers, used in an intelligent fashion. Of course, a high proportion of skill and judgment, particularly in meteorological matters, are involved. The balance between science and art varies from one pilot to another, but the proportion of the former is inevitably fairly high if the maximum benefit is to be extracted from the machine and the atmosphere.

Atmospheric Energy

During a cross-country flight, a glider dissipates energy at an average rate of about 3½ to 4 horsepower. Apart from the small amount of energy provided by the initial launch, this must be made good from energy sources in the atmosphere. The practical sources of mechanical energy in the atmosphere were described by Lord Kelvin over sixty years ago: in effect, the motions of the air must vary with position or time, or must have a vertical component.

So far, it has not been found practicable to use the unsteady motions of the atmosphere or wind shear, and the glider pilot is therefore concerned with sufficiently extensive regions of the atmosphere in which there are vertical components of the air velocity, appreciable in both magnitude and duration. Ultimately, the mechanical energy in the atmosphere is derived from the sun; it therefore follows that, if one regards soaring as the use of energy available in the atmosphere to carry out sustained flight, a logical development would consist of using solar energy in a more direct form. Dr RASPET[1] has shown that this might be a feasible development, using solar cells in the upper surface of the wing, but at the moment such ideas are speculative.

At present, there are three types of air motion exploited by glider pilots:

(*1*) '*Hill lift*'—due to the vertical component of air velocity which occurs on the windward side of a hill or ridge.

(*2*) '*Standing waves*'—due to a ground feature producing a relatively extensive atmospheric disturbance. The ground feature need not necessarily be a hill—it could be the leeward edge of a plateau, for example. Under suitable conditions, the disturbance extends to a height which may be large compared with that of the ground feature and to a considerable distance leeward, often in the form of a series of vertical waves in the streamlines of the airflow. This phenomenon has been extensively explored both in practice and theory[2].

Both of these forms of atmospheric disturbance are substantially stationary relative to the ground and there is often no clear distinction between them.

(*3*) *Thermal currents*—In the presence of sunlight, the ground becomes heated and transfers some of this heat to the adjacent air. When a parcel of air attains a temperature in excess of the general ambient temperature, buoyancy forces will cause it to rise and it will continue to do so until its temperature, decreasing adiabatically, becomes the same as that of the surrounding air. The height it will attain clearly depends on the atmospheric lapse rate. If the initial moisture content and the height attained are sufficient, the moisture will

condense to form cumulus cloud. Although thermals have been used for soaring for about thirty years, it is only quite recently that a really satisfactory theory explaining their detailed structure has been suggested[3].

Most cross-country flights in gliders are carried out using thermal currents only, but some spectacular results have been achieved under favourable conditions by the use of standing waves (*e.g.* H. C. N. Goodhart's flight of 360 miles from Lasham, Hants to Portmoak, Inverness). It is customary, therefore, to design the machine and the instrumentation primarily to exploit thermals.

The Use of Thermals

Before describing the considerations involved in these aspects of design, it is important to consider how thermals are used to carry out cross-country flights.

Figure 1 shows approximately the performance curve or ' polar ' for a modern glider, the Slingsby *Skylark 3F*, in which the sinking speed in still air is plotted as a function of forward speed. Strictly speaking, both speeds are ' equivalent airspeeds ', and only correspond to true speeds at sea level. For the present purposes, no great error will be introduced by neglecting variations in air density.

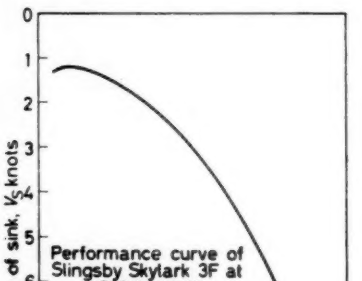

Figure 1

It will be seen that the sinking speed has a minimum of about 1·1 knots at a forward speed of 37 knots (it is convenient to use knots as the unit of vertical speed, rather than the more conventional ft/min, to simplify calculations of gliding angle) and hence if the glider is flown in a region in which the air has a vertical component of velocity greater than 1·1 knots, the glider will ascend relative to the ground. In practice, since a thermal has a fairly restricted cross-sectional area, the glider must be flown in circles in order to remain in the region of rising air. To carry out a cross-country flight, the process consists of climbing in a thermal, gliding in a more-or-less straight line to the next thermal, inevitably losing height on the way, and repeating this process as long as the weather, the pilot's skill or the size of the country permit. The skill is involved in achieving the best rate of climb in any one thermal and in assessing where the next one is likely to be situated.

Speeds

It is clear that the glider should be flown at the speed giving minimum rate of sink whilst climbing in the thermal. However, since the polar relates to straight flight, the appropriate airspeed and the corresponding minimum sinking speed would both be slightly increased in circling flight, compared with the figures quoted above.

In performing a cross-country flight, the pilot will normally be interested in achieving the maximum average speed. Even if he wishes to cover the maximum distance, as opposed to achieving the maximum speed over a fixed distance, he will usually work on the assumption that the distance will be limited by the number of hours in the day for which suitable thermals exist. Special circumstances may arise in which the pilot becomes more interested in gliding angle relative to the ground, but this often only arises as a dependent variable. In zero wind, his ground speed whilst circling in a thermal would be zero, whilst between thermals it would be the same as his cruising speed. The mean speed will therefore be far less than the inter-thermal cruising speed.

It is easy to see that an optimum inter-thermal speed will exist: if the pilot flies too slowly, he will waste time in getting to the next thermal; if he flies too fast, he will waste height in getting to the next thermal and will have to spend a longer time in the thermal to regain height. An analysis can easily be made of an idealized flight consisting of a series of climbs and straight glides, as shown in *Figure 2*.

It is also necessary to take down-currents into account for, if part of the atmosphere is ascending in thermals, other parts must be descending outside them. In practice, the down-currents are usually concentrated around the thermals. However, it is convenient to assume an average rate of descent of the air between the thermals.

A simple calculation[4] shows that the construction of *Figure 3* gives the best cruising speed between thermals and the maximum average speed attained.

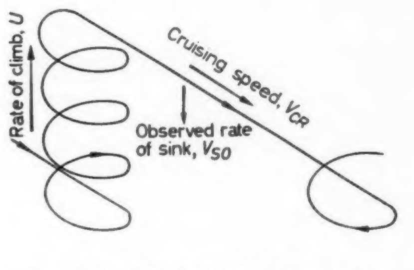

Figure 2. Section of an idealized cross-country flight

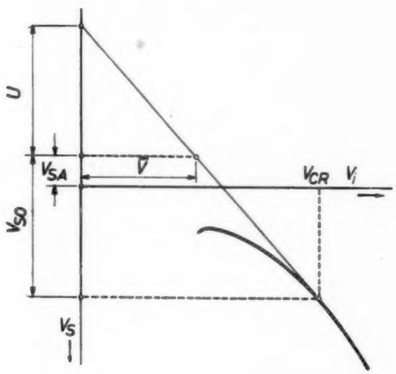

Figure 3. Construction to find the best cruising speed between thermals, using the glider performance curve: V_{SA}=mean rate of descent of air between thermals; $\bar{V}$= average cross-country speed; other symbols are explained in Figure 2

It will be seen that the best cruising speed for a given glider is determined by the sum of two quantities which can be observed by the pilot: the achieved rate of climb in the thermals and the achieved rate of descent between them. This fact forms the basis of a simple device for displaying the best cruising speed of the pilot. If the instrument indicating rate of climb and descent (the 'variometer') has a linear scale, it may be fitted with a movable verge ring. On the basis of the construction of *Figure 3*, this verge ring can be calibrated so that the pointer indicates the speed at which the glider ought to be flown under the conditions prevailing at any instant when cruising between thermals, the datum of the verge ring having been set to the achieved rate of climb in the thermals (*Figure 4*).

It is clear that since this analysis applies to the flight as a whole, it will not necessarily give the maximum attainable speed for a flight under given conditions if applied piecemeal to each climb-plus-glide section of the flight, since conditions may vary as that flight proceeds. However, in the absence of exact foreknowledge of conditions to be encountered in the future, the pilot must proceed on a thermal-by-thermal basis. In practice such a procedure is unlikely to lead to any appreciable loss in performance since the average speed attained is fairly insensitive to variations in inter-thermal cruising speed.

This technique still applies in the presence of a wind, but the ground speed is then increased or decreased by the component of wind velocity along the mean track of the glider.

The Optimum Glider

From the piloting point of view, it will have been noted that a knowledge of the actual rate of ascent of the air in the thermals is not required: the pilot only needs to know the rate of climb of the glider. Since this quantity is the difference between the rate of ascent of the air and the sinking speed of the glider through the air, the designer will naturally wish to keep the latter as low as is reasonably feasible. The rate of sink of the glider through the air when circling in a thermal will be rather greater than the minimum rate of sink in straight flight, partly as a consequence of the effective increase in wing loading and partly due to various minor effects arising from the control deflections and the non-uniformity of forward speed across the span. A factor of 1·5 would probably be of the right order under normal conditions.

Again using the construction of *Figure 3*, it is now possible to construct a curve of average cross-country speed against thermal strength for a given glider (*Figure 5*). It is obvious that the cross-country speed will be zero when the thermal strength just equals the sinking speed of the glider when circling, for then it can just maintain height by staying in the thermal.

If a tangent is drawn to this curve from the origin, it will be clear that the point of tangency represents the conditions at which the glider is operating most efficiently, since the ratio of cross-country speed to thermal strength is then a maximum. The corresponding thermal strength will then represent the 'design thermal strength' for the

machine. The slope of the tangent represents a 'figure of merit' for the glider and, being dimensionless, is influenced by the *shape* of the polar curve and, in particular, by the best gliding angle. It therefore follows that the 'figure of merit' does not depend on dimensional quantities such as the wing-loading of the glider. Altering the wing-loading of a glider will produce a series of curves of the type shown, of which the envelope will be the tangent already drawn. It therefore follows that, ideally, the wing loading of a given glider should be adjustable so that it is always operating at its 'design thermal strength'.

In practice the required variations in wing loading (hence in all-up weight) to meet this condition are quite excessive, since doubling the design thermal strength would involve a four-fold weight increase. Gliders have been built with water-ballast tanks, but structural considerations limit the amount of water which can be carried to such an extent that it is scarcely worthwhile, and in any case, the loss in performance involved in flying at a wing loading different from the ideal figure is quite small. Thus, with water ballast, the all-up weight of the *Breguet 901* is 875 lb. The corresponding design thermal strength is 372 ft/min. Without water ballast, the weight is 705 lb and the design thermal strength is 335 ft/min. If, however, it were flown at the lower weight in the stronger thermals, the loss in average speed would only be about half a knot.

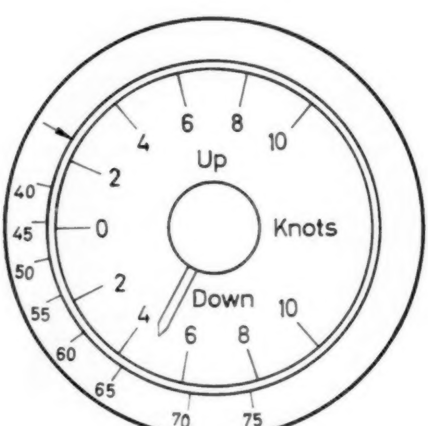

Figure 4. Variometer fitted with verge ring giving best speeds to fly. The datum has been set to about $2\frac{1}{2}$ knots, the mean rate of climb in the previous thermal. For the rate of descent shown, the glider ought to be flying at 67 knots

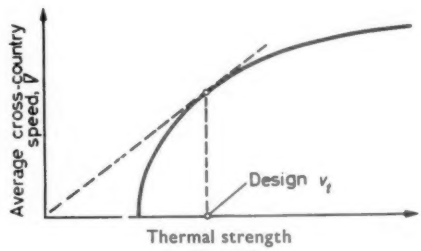

Figure 5

However, it does follow that in broad terms the principle of design consists of achieving a clean machine with a good value for the best gliding angle and a wing loading to suit the *average* thermal conditions under which it is to operate. In this country a wing loading of 4·5 lb/ft² would be usual, corresponding to a 'design thermal strength' of about 370 ft/min. Under more favourable conditions, higher wing loadings would be appropriate and figures as high as 8 lb/ft² are by no means unusual in the U.S.A.

Design Trends

These considerations, together with the load to be carried and the nature of the structural materials used, determine in broad outline the major features of the design. In order to keep the profile drag low, the boundary-layer is kept laminar over as much of the surface as possible. Low-drag aerofoil sections are used: surprisingly enough, these are often quite thick, in order to give both a light structure and low drag over a wide speed range. Careful attention is paid to keeping the surface smooth and free from ripples. Some modern wings are so good in these respects that they look more like wind-tunnel specimens than real structures.

Efforts are made to keep the wetted area small, so that most modern gliders look elegantly slender in all directions. In some machines, the pilot reclines almost as on a couch in order to reduce the fuselage diameter, but it then becomes difficult to achieve comfort and a good view simultaneously. To reduce the induced drag, the span loading is kept small: the actual span therefore tends to be quite large and many high-performance machines have spans between 60 and 65 ft. Since the wing area is to be kept as small as possible, in order to reduce profile drag, the aspect ratio (span/mean chord) is frequently of the order of 20. A typical modern British glider is shown in *Figure 6*.

Gliders as big as this are distinctly inconvenient objects from all points of view, but this is the size which emerges when conventional wooden or metal structures are used. Reduction in size is only possible by further aerodynamic refinement or by making the structure more efficient. Without introducing radical innovations (*e.g.* solar batteries, boundary-layer control), aerodynamic refinement has already been taken so far that only limited gains are likely in this direction. The possibilities mentioned do not yet show any signs of being practicable.

In the structural field, considerable possibilities exist. Until recently, glider structures were surprisingly primitive in concept by current aeronautical standards, however excellent the craftsmanship. Latterly, increasing use has been made of various types of sandwich construction, some incorporating plastics, and there are signs that the size of high-performance gliders may be diminishing.

Instruments

Most gliders are fitted with a straightforward array of aircraft instruments including an artificial horizon and turn-and-slip indicator to permit cloud-flying. Since the power for gyro instruments must come from batteries, efforts are made to keep their power consumption low. A directional gyro is not normally carried, an excellent substitute being a special compass designed to be free from the usual turning errors. Since the pilot is vitally interested in his rate of climb or sink, suitable instrumentation is particularly important.

The conventional 'variometer' effectively measures the pressure difference across an orifice due to air flowing out of or into an insulated vessel as the glider ascends or descends. The time-constant of a mechanical variometer tends to be of the order of a few seconds, so that its interpretation may be a matter of some complexity. When cruising between thermals, this slow response may be an advantage, and a mechanical variometer equipped with a suitable verge ring as described previously is often used for this purpose. When circling in thermals a faster response is useful to enable the pilot to locate the region of greatest vertical velocity as quickly as possible. Various electrical variometers have been developed, in which the flow into or out of the insulated vessel is detected by differential cooling of thermistors.

If the variometer is connected to an insulated vessel and a source of static pressure, the instrument strictly indicates rates of change of outside air pressure. For convenience, the dial is calibrated in terms of rate of change of height, assuming the standard sea-level relationship between air pressure and height. If for some reason the glider is caused to lose speed, the instrument will show a decreased

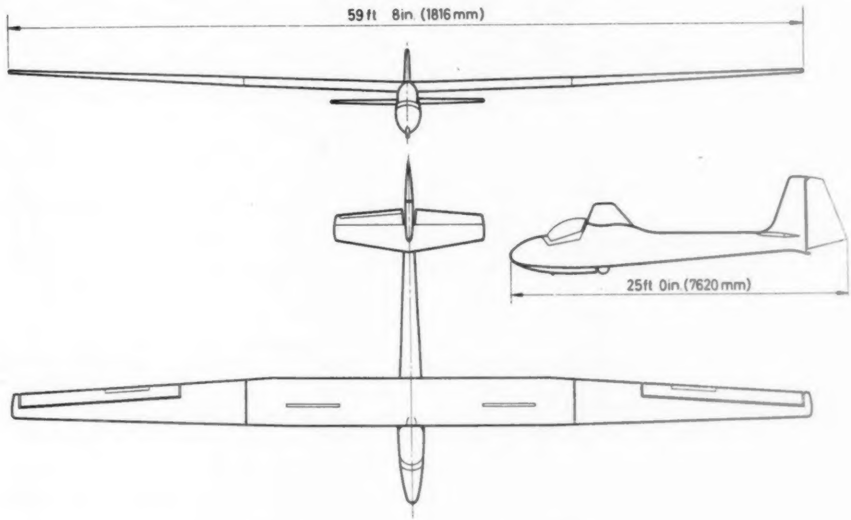

Figure 6. General arrangement drawing of Slingsby Skylark 3F. (Courtesy Slingsby Sailplanes, Ltd)

Figure 7. Slingsby Skylark 3F. (Courtesy Slingsby Sailplanes, Ltd. Photo C. E. Brown)

rate of sink or even a rate of climb. Such an indication can be rather confusing to the pilot, who may have difficulty in distinguishing between variations in rate of climb from this cause and those due to vertical motions of the atmosphere, particularly in rough conditions. It can be shown that if the variometer is connected not to a source of static pressure but to a venturi providing (static pressure less dynamic head), the indications of the variometer will be a measure of the rate of change of the total energy (*i.e.* potential energy and kinetic energy) of the glider. Since the total energy can only be increased by extracting energy from the atmosphere, this arrangement eliminates spurious indications due to minor variations in the speed of the glider. A more sophisticated arrangement effectively varies the volume of the insulated vessel by means of the pitot pressure used to operate the airspeed indicator[5].

The major problem in soaring is the location of thermals. On some days this may present little difficulty, but on many occasions it is easy to waste time in finding a thermal even when the approximate position can be inferred from the adjacent clouds. On cloudless days, there is often very little guide indeed to their presence. Some efforts have been made to locate thermals at a distance by measuring the difference in the temperature of the air at the wing tips. This method is open to a number of theoretical objections and has not been of practical consequence so far. Some effort is currently being applied to the detection of horizontal potential gradients in the atmosphere, a method which may have more possibility of success.

Conclusion

Different pilots may achieve success in sporting gliders by employing various proportions of science and inspiration, according to their knowledge and temperaments. As with any complex process involving rapid decisions and incomplete data, a considerable element of informed inspiration is always necessary to perform really great feats. Soaring is still a young sport compared with, say, sailing but it enjoys many technological advantages, often as a by-product of the immense efforts lavished on ' real ' aeroplanes. The consequence is a sport which applies the resources of wide fields of modern technology to provide a singularly rich variety of experiences to its exponents.

References

[1] Raspet, A. *Swiss Aero-Revue* Feb., 1960
[2] Scorer, R. S. *Quart. J. R. met. Soc.* (1953) **79**, 70
[3] Woodward, Betsy. *Swiss Aero-Revue* June, 1958
[4] Welch, A. and L. and Irving, F. G. London: *The Soaring Pilot* John Murray 1955, 34
[5] Irving, F. G. *Swiss Aero-Revue* June, 1957

THE RIGHT HONOURABLE

RONALD MORCE WEEKS,

K.C.B., C.B.E., D.S.O., M.C.

first Baron Weeks of Ryton

LORD WEEKS died in London on August 19th; he was 69. He first came to the public eye as captain of the University of Cambridge Association Football team in 1912. After serving with distinction in the Rifle Brigade in the First World War he returned to the Glass Works of Pilkington Brothers and, in 1939, became Chairman. Between the wars he took an active and enthusiastic interest in the affairs of the Territorial Army and at the outbreak of the Second World War became a divisional staff officer in the field. His career in the army was remarkable and indeed unique for an ' amateur ' soldier for when the post of Deputy Chief of the Imperial General Staff was created in 1942, he was appointed. He ended as Deputy Military Governor and Chief of Staff to the Control Commission in Germany.

Weeks returned to Pilkingtons in 1945 and later in the year joined the board of Vickers becoming Chairman in 1949. His period as Chairman of Vickers until he retired in 1956 was a period of turmoil, expansion and diversification of the interests of one of the largest industrial groups in the country. When he ' retired ', he went to work in many ways, as Chairman of the Finance Corporation of Industry, as a member of the boards of various companies: in Vickers he interested himself in projects for the exploitation of nuclear energy. He was Treasurer of the Industrial Fund for the Advancement of Scientific Education in Schools, he was a Trustee of Churchill College. His experience of national and industrial affairs on the one hand and of educational matters on the other was almost alarming in its comprehension.

No man without immense drive could of course have achieved what Weeks did. Certainly he had drive but he was anything but a steam-roller. He enjoyed it. He had a methodical, probing, adventurous mind to which a new discovery, a new career, the organizational mountain of army supply in 1941, the supply of scientists and technologists after the war—all were a challenge. He joined the *Scientific Advisory Board* in 1958. From his career we might have expected a restless pontiff. We met a calm, enthusiastic almost studious recruit who after some turgid discussion would say quietly ' I think so and so is the man to help on this '. And invariably the help came. Granitic qualities of character—combined with startling blue eyes—are rarely associated with a human personality and a roving, rigorous intellect. The pity is that we had his advice for so short a time.

SURVEY

Conserving Water

Loss of water by evaporation from open reservoirs is a problem not only in the acknowledged 'arid' regions of the world, but also, more surprisingly, in some parts of this country, where the annual loss may be as much as 18 in. Though a complete solution has not been found, much research has already been published and a classified bibliography* of literature on water conservation is available.

Much of the pioneering work on evaporation control has been carried out in Australia, and some time ago *Research* published a report† on the studies of Mr. W. W. MANSFIELD of C.S.I.R.O., Melbourne, on the application of monomolecular layers of cetyl alcohol (hexadecanol) to large water surfaces. Last year C.S.I.R.O. tested a new technique in which trails of a finely powdered cetyl-stearyl alcohol blend are blown over the reservoir surface from a boat carrying a grinder–duster developed by Mr C. S. ROBERTSON of the Broken Hill Water Board.

Figure 1. Boat equipped with the Robertson grinder–duster, used on Umberumberka Reservoir, Australia

The method is recommended for storages over 150 acres in area. In wind velocities under 5 m.p.h. it has been found to reduce evaporation by up to 50 per cent. Uniform spreading of the film is assisted by laying the trails in a crosswind.

A technique suitable for storages up to 1 acre in area has been developed by a British commercial firm which co-operates with C.S.I.R.O. Price's (Bromborough) Ltd have made a submerged constant-feed dispenser for the solvent method of film application. Of the conventional solvents tested by Price's kerosene, the cheapest, was found to be the most efficient for giving stable cetyl alcohol films.

* Water Conservation Bibliography, Technical Publication No. 7, Price's (Bromborough) Ltd. † *See* Research (1957) **10**, 198 and 291

Wind has a most important effect on film efficiency. While steady winds of low velocity help to spread the film as it is formed, squally gusts disperse it and, when the powder method is used, the resulting rough water causes wetting of the powder with resulting loss of spreading power. In a series of tests carried out on Loch Laggan in Inverness-shire a relationship between wind velocity and speed of film movement has been found, making it possible to estimate the minimum rate at which cetyl alcohol must be added to the water surface, under given conditions, to maintain an effective film. It was also found in these investigations that the rate of film movement, even in a steady wind, is not constant, but accelerates progressively. This fact, hitherto unsuspected, opens up a new field of research.

Flight Observer

After any air crash there is always an investigation to discover the cause but sometimes the cause has been untraceable. It could now be recorded by a new electronic aid which has been developed by Hawker Siddeley—a steel cased miniature tape recorder, only 13 in. by 6 in. by 6 in., weighing 66 lbs, which has apparently survived crashes at as much as 250 m.p.h. The armour plated casing withstands fire but the tape will melt at 150°C.

Littoral Drift

The coastal engineer needs to know the rate of 'littoral drift', *i.e.* the rate at which pebbles or sand drift along the coastline; in the past estimates have been made by measuring the accumulation against obstacles—large groynes or harbour breakwaters—but a new method has been devised by the Hydraulics Research Station, using fluorescent tracers.

The most satisfactory tracer so far developed is *Rhodamine B*, which glows with a strong red fluorescence when placed under ultra violet light; this is incorporated in artificial pebbles made of concrete and plastic glue, adjusted to the right density by using a heavy aggregate such as quartz-dolerite and broken into lumps whose sizes approximate to the pebbles on the beach being investigated; or it is mixed with beach sand and plastic glue, and when hard ground back to the grain size of the sand. The pebbles or sand are then dumped on the beach and periodic surveys made to check their rate of spread—the pebbles are visible on the beaches at night under ultra-violet light, and can be counted at check points, whereas with sand it is necessary to take samples from such points and analyze them in the laboratory.

BOOK REVIEWS

Recent Research in Molecular Beams

A Collection of Papers dedicated to OTTO STERN on the occasion of his seventieth birthday

IMMANUEL ESTERMANN (*Ed.*)

(*190 pp; 9¼ in. by 6 in.*)

New York and London: Academic Press. $6.50, 52*s*

Half a Century of Molecular Beams

IN THESE days when the daily press reports on an atomic accelerator which for a few minutes produced a beam of protons with energy slightly more than 30,000 million electron volts, it is wholesome to be reminded of the part which beams of neutral atoms and molecules moving with thermal velocity of, say, one electron volt, have played in modern physics. These molecular beams are still the cinderella of the physics curriculum of our universities, although half a century has now nearly gone since Louis DUNOYER in 1911 first demonstrated in a planned laboratory experiment the collision-free travel of molecules in a straight line through a vacuum. Vacuum technique was then in its infancy and electronics very little talked of. In the early 1920's Otto STERN with great single mindedness of purpose developed the molecular beam technique into a tool of beauty and simplicity in principle for the investigation of the properties and behaviour of individual molecules in their normal state.

In the early experiments the beam was detected by condensation of the atoms and molecules on a target. A good deal of effort in the 1920's was devoted to the development of other quantitative methods, but the production of sufficiently intense beams and the use of sensitive detectors for such low-energy particles has always remained the crucial experimental problem.

The achievements with the molecular beam method have led to the award of three or four Nobel prizes. Stern himself has laid one of the cornerstones of quantum theory by giving, together with Walther GERLACH, direct experimental proof of the space quantization of the magnetic moment of the atom. Even with the weakest magnetic field the magnetic moment must be either parallel or antiparallel to the direction of the field. The experimental proof of 'flip-over', the reorientation of the spins during a non-adiabatic change in the direction of the magnetic field, laid the foundation for Isidore RABI's ingenious device of the molecular beam magnetic resonance method.

Thus, a precision method for the measurement of magnetic moments was created. It is now generally accepted that the magnetic moment of the proton is +2·792743 nuclear magnetons, but it is well to remember that Stern had been able to show conclusively five years earlier that the magnetic moment of the proton was, within an accuracy of about 10 per cent, 2·5 nuclear magnetons. Another milestone was the determination of the de Broglie wavelength of a beam of helium atoms to within 1 per cent.

For a quarter of a century now the centre of gravity of molecular beam work has moved from Europe across the Atlantic, but the one practical application of the molecular beam method, the 'caesium clock' with its accuracy of one part in 10^{10}, has been made in this country by Louis ESSEN.

Dr ESTERMANN is to be congratulated on having seized on the occasion of Otto Stern's seventieth birthday to invite a number of American physicists to contribute to the volume under review. By its nature a collection of articles on such widely different topics as 'Molecular beam research in Hamburg, 1922–33' (I. ESTERMANN), 'Molecular and atomic beams at Berkeley' (W. A. NIERENBURG), 'Velocity distributions in potassium molecular beams' (P. M. MARCUS and J. H. MCFEE), 'Electron magnetic moments and atomic magnetism' (V. W. HUGHES), 'Hyperfine structure measurements in the metastable 2S state of hydrogenic atoms' (P. KUSCH), 'Shapes of molecular beam resonances' (N. F. RAMSEY), 'Comparison of methods for the determination of nuclear spin as applied to radioactive nuclei' (V. W. COHEN), 'Molecular scattering at the solid surface' (F. C. HURLBUT), 'Some applications of molecular beam techniques to chemistry' (S. DATZ and E. H. TAYLOR), 'A Stern–Gerlach experiment on polarized neutrons' (J. E. SHERWOOD, T. E. STEPHENSON and S. BERNSTEIN) does not make for easy reading and can be no more than an appetizer. However, it holds out the hope that in the right person's hands a break through will be made with the molecular beam technique in the fields of chemical kinetics and catalytic reactions. R.S.

Mechanical Properties of Intermetallic Compounds

J. H. WESTBROOK (*Ed.*)

(*ix + 435 pp; 9¼ in. by 6 in.*)

New York and London: John Wiley. $9.50, 76*s*

THIS volume in the Electrochemical Society Series is the record of the papers and discussion at an international symposium held during the 115th meeting of the Society at Philadelphia, May 3–7, 1959.

Interest in intermetallic compounds has been stimulated recently in two ways. One is the discovery that these compounds include an extensive range of semiconductors, some of which will very likely find important applications in electronic devices. The other is the urge to find superior constructional materials to meet the advancing requirements of military and space equipment, and of industrial processes. The latter was evidently the spur for much of the work reported in this volume, but semiconductors are not entirely neglected for there are also two interesting chapters specifically devoted to the plastic and electromechanical properties of the important intermetallic semiconductor indium antimonide.

Most of the papers originate from laboratories in the U.S.A., but international participation is evidenced by British, German, Russian and Japanese contributions. The book opens with a well referenced review of the literature. This is followed by papers on the influence of electronic structure on mechanical strength; effects of temperature on the mechanical properties; experimental techniques such as tensile and torsional testing

and extrusion; fractographic studies; and the influence of defects. The final seven papers deal with various aspects of the properties of specific compounds.

This is a well produced volume with large type and clear diagrams and photographs. As an up-to-date account of various research items recently in progress it should be of particular value but, like other conference reports in new and rapidly developing fields of work, a great deal of the contents may date very quickly. The book is enhanced in value by the inclusion of the discussion on each paper. It is certainly a volume that should be available in libraries for reference purposes, but the price is high and only the specialist would be recommended to invest in a personal copy. V.R.

Technique of Organic Chemistry. Vol. I. Physical Methods of Organic Chemistry, 3rd Edition. Part II.

A. WEISSBERGER (*Ed.*)

(*xii+903+21 pp; 9¼ in. by 6 in.*)

New York and London: Interscience Publishers. 184*s*

PART I of Volume I of *Weissberger* was reviewed in these columns recently (this volume, p. 244). The plan of the volume, discussed there, envisages a first volume composed of four parts; the present work is the second of these parts.

The point was made, in connection with Part I, that the title of this volume is misleading, and that it is useful to physical and inorganic chemists as much as to their organic colleagues. If that was true of Part I, it is an even more noticeable fact about Part II. It is doubtful if even the new species of chemist who would admit to the description 'organic' will find very much here to match against his laboratory experience, and the almost extinct 'classical organic chemist' will recognize no landmarks—with the possible exception of the one labelled *Refractometry*. To press the current classification one stage further, it would be fair to say that much of this book is mainly for the chemical physicist.

The topics dealt with are 'Determination of Diffusivity', 'Determinations by the Ultracentrifuge', 'Refractometry', 'Determination of Crystal Morphology', 'Crystallochemical Analysis', 'Light Microscopy', 'Microspectroscopy', 'x-ray Microscopy', 'Electron Microscopy', 'x-Ray Crystallography', 'Electron Diffraction by Gases', and 'Neutron Diffraction'. The space allowed to these topics varies considerably; thus, the first three have from 112 to 144 pages each, whilst the rest vary between 24 ('Electron Diffraction by Gases') and 98 ('x-Ray Crystallography') pages each. The lengths of the articles bear no obvious relationship to the relative importances of their subjects. Indeed, it is not clear at all on what basis the available space has been shared out. With such varied treatment of such a wide range of topics it is obvious that only long use of the book will prove what is really useful.

Part II has followed Part I with commendable speed, and organic chemists in particular will hope that the remaining parts, which promise discussions of some topics nearer to their own interests, will not be long delayed. K.S.

The Arc Discharge

H. DE B. KNIGHT

(*xix + 444 pp; 8¾ in. by 5½ in.*)

London: Chapman and Hall. 63*s*

THE arc discharge has long been a subject of great interest in physics, and particularly during recent years in the attempts to attain controlled high temperatures. However, the important role which the arc discharge plays in power engineering, especially in the switches and contacts which control electrical power circuits, must not be forgotten. Efforts of power engineers have long been directed to the suppression of arc discharges, or to their rapid extinction when once produced, and to arc control in rectifier valves.

The Arc Discharge by H. de B. KNIGHT deals mainly with the electrical arc in relation to the use of discharge valves, such as Thyratrons, Ignitrons and Excitrons, in which the current is controlled by grids. Although the main purpose, that of an account of the use of an arc discharge valve for the control of electrical power, is always kept well to the fore the author realises that a discussion of the physical principles of the production, maintenance and extinction of an arc discharge must form an important part of any book which is to deal adequately with the subject. He has divided his treatment into three parts: Part I, General Principles, Characteristics and Construction of Tubes (100 pages); Part II, Physical Processes in the Discharge (132 pages); and Part III, The Valve in Use (177 pages). While this arrangement may have certain advantages to the practising engineer, it seems to the present reviewer that Part II follows naturally from the introductory Chapter I, in which the author gives an outline of the discharge, then, having dealt with basic principles, an account of practical applications would conveniently follow. The elementary discussion of the basic physics is mainly qualitative and briefly outlines ionization and de-ionization processes, discharge characteristics and space discharge sheaths. This account, together with a more detailed account of actual valve designs, gives a broad picture of the subject which should be very valuable to the valve designer.

Accounts of tube design, the tube as a circuit component, control methods, discussion of specification, rating, operation, and maintenance of arc tubes are complete, as, indeed, was to be expected from one who has devoted so much of his time to the study of the arc and its applications in the research laboratories of British Thomson-Houston Company. Together with its comprehensive index and bibliography, the book will make a strong appeal to the electrical engineer concerned with power control, and has much of interest to those concerned with valve design and manufacture, to which it can be thoroughly recommended. The book is well produced and copiously illustrated. F. Ll.-J.